S O M E S O R P T I O N S T U D I E S

O N

N Y L O N A N D W O O L

A Thesis
submitted to the University of Glasgow
for
the Degree of Doctor of Philosophy
in
The Faculty of Science

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Technical Chemistry Department,
Royal Technical College,
Glasgow.

Dated the 12th Day of May, 1950.

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II : Results and Discussion (continued)

Acknowledgments

Thanks are due to many members of the staff in The Technical Chemistry Department of the Royal Technical College, including the glassblower, Mr. Barbour, and Messrs. Clunie and Scally of the workshop, for their assistance in constructing the apparatus used in the present research.

The work was carried out under the guidance of Dr. C.H. Giles and Prof. W. M. Cumming, O.B.E., F.R.S.E., and the author is grateful to them for all their help. The author feels particu-:larly grateful to Dr. C.H. Giles, who had a great inspiring influence.

The author also wishes to thank Prof. P. D. Ritchie, successor to Prof. Cumming, for his kind help and suggestions.

Part of the work on the sorption of aqueous phenol on nylon was done by Miss Margaret Laidlaw and Miss Patricia Brand, and the author is indebted to them for their assistance.

Finally, the author wishes to thank the management of the Delhi Cloth and General Mills Co.Ltd., Delhi, India, for granting him the necessary leave of absence, and funds to carry out the present work.

V.B.C.

Preface

This research was originally undertaken with a view to studying sorption on textiles from the vapour phase. This required the use of high vacuum technique and as some free time was available in the initial stages of building up the apparatus, sorption from aqueous solution was also studied.

There are two features of the experimental technique which need particular mention. Firstly, the use of Pyrex glass spirals for sorption measurements from the vapour phase.† A com-:munication to "Nature" in this connection awaits publication. Secondly, the technique of studying vapour phase sorption at temperatures as high as 120°C to 150°C on textile fibres is some-:what novel. It was found that nylon and wool are not damaged even at such high temperatures, if under a high vacuum.

It is hoped to publish the present work in one or more papers in one of the scientific journals.

† Published: May 6, 1950, in 'Nature'.

V.B.C.

ABSTRACT OF THESIS

A review is made of the present knowledge of the subject of sorption in relation to textile fibres and it is pointed out that the exact role of the amino and amido groups of the polyamide or protein fibres in their behaviour with hydroxylic compounds, acids or acid dyes is not yet fully understood. The experiments were planned and the results are discussed to throw additional light on this behaviour.

Sorption has been studied both from aqueous solution and from the vapour phase. The sorbates used were hydroxylic, phenolic or acidic compounds. The fibres used as sorbents included drawn, undrawn and powdered nylon, and untreated, acid treated, dyed and deaminated wool, respectively.

Sorption from aqueous solution

The methods used for the study of sorption from aqueous solu-:tion are those commonly employed, with the difference that in this work, the material : sorbate ratio (and not the material : liquor ratio) was maintained constant. Such a procedure is more in keeping with the requirements of the law of mass action. The equilibrium concentration of the sorbate bath is expressed as 'relative concentration' which is defined as the actual concen-:tration divided by the solubility at the temperature under study. It is shown how results so expressed are thus made easier of

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interpretation and more consistent. The following conclusions are drawn:-

(i) Resorcinol has a greater affinity towards nylon than phenol.

(ii) In spite of its extremely low solubility in water, benzoic acid shows an appreciable sorption on nylon, whereas benzene sulphonic acid shows none. It is concluded that the former combines with nylon by hydrogen bonds at the -NH.CO- groups.

(iii) A formula is derived for the isotherm of phenol on the assumption that the molecules of phenol behave as gas molecules and the solvent water is in effect an indifferent medium. The derivation of the formula then follows the kinetic considerations of Langmuir and the isotherm equation is similar to his equation. From a study of the isotherms at different temperatures, heats of reaction of phenol on drawn and undrawn nylon are calculated and it is shown how swelling and contraction complicate the interpretation.

(iv) The data of rates of sorption have been utilised to calculate the activation energy of a sorbate on the fibre under investigation. This is done by drawing slopes to the rate curves at the zero point and thus calculating the velocity constants at different temperatures. The effect of variations in solubility

with temperature are taken into account by dividing the velocity-constant by the solubility at the given temperature. Energies of activation thus calculated are given for phenol and benzoic acid. The activation energy of phenol on drawn nylon is about 18,000 cal/g.mol. whereas that on undrawn nylon is about 24,000 cal/g.mol. The energy of activation of benzoic acid on drawn nylon is about 25,000 cal/g.mol.

(v) Isotherms of aqueous aniline on drawn nylon revealed an appreciable sorption of this compound by the fibre. It was later discovered that aniline from the vapour phase is not adsorbed by the fibre. It is suggested that aniline combines with nylon not directly but through a bridge of water molecules.

Sorption from vapour phase

McBain and Bakr's spring balance has been used for the study of sorption from the vapour phase. The cleaning of the fibre surface was done under high vacuum (10^{-4} mm.). Spirals of Pyrex glass have given very satisfactory service. The following conclusions are drawn:-

(i) Water and methyl alcohol are attached to nylon and wool by hydrogen bonding on the -NHCO- groups. The present results thus seem to be more in agreement with Cassie's views rather than

with those of Frey and Walter, who assume that the water combines with the polar side chains.

(ii) Water isotherms on untreated wool, acid treated wool, dyed wool and deaminated wool, respectively, show the remarkable result that all these fibres give identical isotherms. The in-:crease in the surface area or the number of amino groups has therefore no direct bearing on the course of water sorption.

(iii) Rates of sorption of dry acetic acid vapour on the dif-:ferent samples of wool mentioned above reveal that the dyed sample (Solway Blue B.S.) shows a far lower rate and the sul-:phuric acid-treated one a far higher rate, than the untreated one. The points of attachment of the dye molecules and the acetic acid molecules appear to be identical.

(iv) Further, sorption and desorption rate studies with acetic acid and benzoic acid vapours on wool and nylon show that the amino group does not exert any specific influence on the course of the reaction, and hence it is concluded that the com-:bination is probably by hydrogen bonds and not by salt formation.

(v) In the case of phenol, β-naphthol, benzoic acid and alizarine, rates of sorption and desorption were studied at temp-:eratures varying from 60°C to 150°C. An important point is that successive sorptions and desorptions cause a loosening of the fibre structure and the fibre thus shows an increasing

capacity to sorb. This is true of both wool and nylon. The sorption in all these cases is quite high and it must be concluded that these substances have a great affinity for the two fibres. The mode of combination is presumably by hydrogen bonds. The energies of activation for the combination with nylon and wool range from 4,000 to 6,000 cal/g.mol.

Adsorption is considered theoretically both from the kinetic and the thermodynamic angle. Various theories of adsorption are discussed and consideration of the various general theories is made with special reference to textile fibres. It is suggested that the "non-rigidity" of the fibre surface is bound to make impossible a perfect fit of experimental results to any theory.

I

INTRODUCTION.

I N T R O D U C T I O N

(i) GENERAL

Sorption studies are of immense value to the understanding of general theoretical chemistry, e.g. in heterogeneous catalysis, colloid science, the structure of active surfaces, the separation and purification of gases, etc. For the textile chemist, the subject is important because it is an aid to the understanding of the internal structure of fibres as well as their behaviour towards dyeing and finishing chemicals. The scope of, as well as the need for, more research in the subject is therefore easily appreciated.

The earlier workers - in the late 19th or early 20th centur-:ies - were greatly hampered by the lack of sufficient data to understand the structure of fibres or their behaviour towards dyes and chemicals. Their work now appears vague and empirical.

But fortunately for us great advance has been made in the knowledge of theoretical textile chemistry during the last 25 to 30 years. This advance has closely followed those made in other branches of chemistry. Thus the conception of electronic valency, the x-ray study of crystalline bodies, new knowledge of the constitution of cellulose and proteins, modern theories of electrolytes, the methods of molecular analysis by means of infra-red spectrum, etc., have all aided the modern textile chemist to design more precise experiments in his own field.

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A review of relevant literature

The literature published by investigators interested in fibre chemistry, shows three main trends in their work:-

(i) Elucidation of the physical and physico-chemical structure of the fibres and correlation of their physical and mechanical properties with their chemical behaviour.

(ii) Formulation of a general theory of the mechanism of dyeing and other textile finishing processes.

(iii) Use of the theoretical basis provided by modern ideas in the fields of chemical kinetics and chemical thermodyanamics.

On the structural side Haworth (1) laid a foundation for cellulose chemistry by developing the cyclic formula for glucose. Similarly Fischer's work on proteins, peptides and amino acids greatly advanced our understanding of the proteinous fibres.

Following Bragg's technique of building up molecular models with the help of x-ray data, Sponsler and Dore (2) established the alternate 1:1 and 1:4 linkages in glucobiose. Meyer and Mark (3) and Polanyi (4) established the question of laterel spacings and put the "molecular chain" theory of cellulose on a firm basis. The fact that these molecular chains could form bundles by lateral cohesion was established by Mark and Meyer (Loc.cit) and by Hengstenberg and Mark (5). This view received further support from the work of Boulton, Dellph, Fothergill and

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Morton (6) who pictured cellulose as a threedimensional network of more or less parallel chain molecules producing "crystalline" regions when orderly arranged and "amorphous" regions when arranged in a disorderly fashion.

Similar fundamental work was taken up by many investigators for studying the internal structure and molecular arrangements within the wool fibre. Of particular interest is the work of Astbury who explained the elastic properties of the wool on the basis of its x-ray structure (7) and established that stretching causes an axial orientation and produces pronounced regularity. Similar evidence for crystalline and amorphous regions in Nylon has now been published by Burns & Garner (8). Marsden (9) and Meridith (10) in two lectures have recently made a very significant contribution by simply and lucidly explaining the importance of the "crystalline and amorphous" nature of fibres and their influence on their dyeing and chemical properties.

As a result of all this work we can now form a general picture of the internal arrangement of molecules within a textile fibre. This picture may be briefly summarised as follows:-

(i) Textile fibres consist of molecules which are very long and thin.

(ii) These molecules are held together by lateral cohesive

forces.

(iii) When the lateral arrangement is of a regular order, the portion of the fibre shows crystalline nature: it resists mechanical extension and also chemical action.

(iv) When the lateral arrangement is irregular the portion of the fibre shows amorphous characteristics. It is easily attacked by chemicals and acquires rubber-like properties - i.e. it offers less resistance to extension.

(v) The crystalline and amorphous regions do not necessar-:ily bear a fixed relation with each other. Depending on the previous history, the fibre may show more or less crystallinity.

(vi) The lateral cohesive forces are of a weak or secondary nature. The modern conception of the hydrogen bond (11) has been widely applied and used by the textile chemists in this connection.

All the x-ray evidence of fibre structure is no doubt con-:vincing. But the real difficulty is to try and provide chemi-:cal evidence to support the x-ray structure. As an example, we may mention one case. Speakman (12), Ender and Müller (13), Harris (14), and various other workers took it as established that the capacity of wool for combining with acids and acid dyes has a stoichiometric relationship with the amount of its free amino groups. But Astbury and Dawson (15) showed conclusively

that the amino groups in the crystalline regions of wool do not show any signs of combination with dyes. Speakman (16) suggests that the electric charges on the amino groups in the crystalline regions are strong enough to attract and hold together dye mole-:cules at a distance and that the dye particles need not actually go near the amino groups in the fibre at all. This argument does not appear to be very convincing.

Speakman's contribution to the understanding of Wool Chemis-:try has however been extensive (17, 18, 19, 20, 21); examples are:- his work on the acid base combining capacity of wool, the sulphide linkage in wool, the relation between its swelling pro-:perties and its physico-chemical structure. Probably one of the most important among his recent contributions is his paper in the Journal of The Society of Dyers & Colorists (22). In this paper he and his colleague (Peters) have applied the Donnan equi-:librium principle to the data of his own titration curves and those of Milton, Harris and his colleagues (23). Speakman and Peters, after pointing out the defects of Harris' theory as well as the improved theory of Gilbert and Rideal (24) have clearly shown how the new application of Donnan's principle explains all the published facts. In Harris' experimental data, the titration curves for hydrochloric acid on wool gradually shifted their position with respect to the pH axis with varying amounts of

pptassium chloride added to the bath. But the two authors have shown that the internal pH within the wool fibre is not the same as the external pH and when this is calculated and the pH - absorption curves are redrawn, all the curves coincide with each other. As far as the theory of the combination of strong acids with wool is concerned, this is indeed a great step forward.

The part played by the amino group in dyeing has been inves-:tigated by Skinner and Vickerstaff (25) from a new angle. They have determined the sorption isotherms of three dyes from aqueous solutions for wool and have indicated that perhaps the dyeing mechanism in protein fibres is more complicated than mere salt formation. Carlene, Fern and Vickerstaff (26) studied the com-:bination of acid dyes with amino and amide groups in nylon fibre and found the behaviour of these groups similar to those in wool.

Some interesting data on the dyeing of direct dyes on nylon have been published by Boulton (27). His observation that nylon can be dyed by direct dyes from a neutral bath as well as by direct or acid dyes from an acid bath is interesting. This shows that nylon can show a dual dyeing behaviour, i.e. dye combines as in cellulose on the one hand and as in wool on the other. Another important observation made by him is that nylon yarn dyed with direct dyes exhibits dichroism when examined in polarised light. As in cellulose, residual valency forces therefore seem to take some part in nylon dyeing.

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The heat changes accompanying dye-absorption or acid absorp-:tion by protein fibres have been calculated by various workers. Thus Harris (28) has studied the effect of temperature on the ti-:tration curve for hydrochloric acid on wool and from the heat calculations finds support to the idea that $-NH_2$ and -COOH groups in wool are completely ionised; but his data could not be taken as giving proof either for or against Speakman's salt-linkage theory. Speakman and Scott on the other hand (29) determined the heats of reaction for hydrochloric acid and acetic acid on wool calorimet-:rically, and from the low heat values obtained, they concluded that the work required to break the salt linkages in wool has to be spent by the incoming combining ions and so the value of heat of reaction is low. This they considered an indirect proof of the salt linkage theory.

It is to be noted here that from the point of view of the work presented in this thesis, this controversy on the exact role of the amino and amido groups of wool and nylon in their combina-:tion with acids or acid dyes is of particular interest. While discussing the experimental data, an attempt will be made to throw some light on this point.

Mention must be made of one more piece of work by Marsden & Urquhart published in 1942. (30). These authors studied the absorption of phenol by cellulose acetate and clearly demonstrated

how the absorption of phenol was closely connected with the absorption of water itself. The swelling action of phenol is explained or assumed to be due to hydrogen bonding between the phenolic oxygen and the carbonyl group of the cellulose acetate. The conception that hydrogen bonding might also play an important role in sorption of dyes and chemicals by textiles, has gained considerable support since then.

From what has been said in the foregoing, it will be clear that data of sorptions from solution have a very important role to play. But these data are not sufficient. There are some inher-:ent difficulties which make it necessary to resort to many assumptions. Moreover when sorption is studied from solutions, the varying solubilities of the solutes at different temperatures makes the effect of temperature on the rate and equilibrium of sorption reaction difficult to ascertain.‡ The heat calculation from such data cannot be taken without some reserve. Furthermore, the part played by the solvent molecules themselves in changing the structure of the fibre or in influencing the course of sorption has always to be ignored for mathematical simplification - and this may not be always right.

As a result of this, the study of vapour sorption on textiles has attracted the attention of many textile investigators in recent times. The enormous amount of work done on the sorption

‡ In the present work some corrections are suggested to overcome this difficulty.

of gases and vapours on active surfaces comes as a very handy aid for the textile investigator. The pioneering work of Langmuir (31) very greatly helped the understanding of the kinetics of sorption and for the first time it was possible to treat sorption phenomena with mathematical precision. Volmer (32) derived an isotherm equation very similar to that of Langmuir but by thermodyanamic and not kinetic treatment. This gave weight to Langmuir's kinetic theory. Fowler (33) derived an exactly similar equation to that of Langmuir and Volmer from purely statistical conceptions. His work again proved the essential correctness of Langmuir's basic ideas. But it also made it clear that Langmuir's 'Condensation-evaporation' mechanism was not to be taken literally. In other words Fowler emphasised the essential thermodynamic character of the equation.

Langmuir equation explained many sorption processes very well. But it could not be universally applied. It simplified matters too much by assuming sorption to be only one molecule thick. Moreover Langmuir's equation can be applied only to a part of the adsorption isotherm and it holds true only in the middle pressure range. Both at very low adsorptions and at very high adsorptions the equation does not apply. Modified theories have therefore been put forward. Thus Polanyi (34) and later Polanyi and Goldman (35) proposed a new theory generally known as the 'Potential Theory'. They assumed that the adsorption was due

to long range attractive forces extending from the surface of the adsorbent. Another older theory of multi-molecular adsorp-:tion (36) was revived in 1920 by Megavack and Patric (37) and is now generally known as the capillary condensation theory. This theory attributes adsorption to condensation of the gas or vap-:our in the fine capillaries of the adsorbent.

A very significant advance was made when Brunauer, Emmet and Teller propounded their new theory of multi-molecular adsorption (38). Their fundamental assumption was that the same forces that are active in condensation are also producing the phenomenon of adsorption. On this assumption they derived an isotherm equation that was a generalisation of Langmuir's treatment of uni-:molecular adsorption. The actual derivations of the Langmuir and Brunauer equations is given in ~~the~~ appendix 1.

Brunauer's theory has a great many advantages over the older theories. It is a good attempt to arrive at a unified theory of adsorption. It describes the entire course of adsorption including unimolecular adsorption and multimolecular adsorption and also capillary condensation.

In the last two or three pages, we have very briefly outlined the theoretical development of the subject of sorption to show clearly how the textile investigator interested in vapour phase sorption of fibres, has a fund of knowledge from which to draw. We shall now attempt a brief account of the available literature

in the field of vapour phase sorption by textile fibres.

Compared with the data on sorption from solutions, there is a paucity of data on sorption of gases and vapours on textile fibres. The only vapour which seems to have attracted wide attention is water vapour. Most fibres have been studied with respect to their ability to sorb moisture. This is done, firstly because it has long been known that the mechanical properties of fibres are greatly influenced by humidity conditions. Secondly the sorption of water by textiles has a very great theoretical significance. If the mechanism of the mode of attachment of the water molecule could be precisely known, it would be a very great help to understand many absorption phenomena and also the internal structure of fibres.

Almost all the important fibres have been studied with respect to water sorption. Thus Sheppard and Newsome (39) made the first suggestion that the hydroxy groups in cellulose are responsible for attracting water molecules during sorption. Urquhart and Williams (40, 41, 42, 43) made an extensive study and found support to the idea that the hydroxyl groups of cellulose are hydrophilic. They also put forth a tentative explanation of the phenomenon of hysteresis. Bull (44) investigated a number of proteins including protein fibres and nylon and found that all the proteins followed Brunauer's isotherm accurately. He calculated the B.E.T. constants and the surface

areas from the water isotherms and also was able to calculate the free energy changes accompanying sorption. He believes that his results corroborate the view that "protein molecules in the solid state are linked together to form coherent planes whose exposed surfaces are hydrophilic. Water is adsorbed between these planes".

In spite of the extensive available data and the suggested theories, the explanation of the behaviour of water towards cellu-:losic, or protein polymers, is still incomplete. Thus the iso-:therm of Pierce (45) has been very strongly criticised by Gilbert (46). He also criticises another isotherm of Cassie (47) and raises doubts of the validity of Brunauer's conception that the molecules of adsorbed water in the second and successive layers are behaving as water molecules in the free state.

New equations for the water isotherm on fibres continue to appear. Thus, very recently Cassie (48) has come forward with a new suggestion, according to which water absorption at high regains must cause an increase in entropy and this in his opinion would eliminate both the capillary condensation theory and the potential theory, which ascribe the absorption to a decrease in the heat content of the system without an increase in entropy. He further accounts for the work of swelling and the energy spent in doing this work and calculates a "stress-free isotherm", showing that such an isotherm loses its sigmoid character. His analysis indi-:cates that the water attracting groups in Keratin are the -CO-

groups, and gives the energy of bonding of water molecules as 6.6 kg. cal. per mole.

Hailwood and Horrobin (49) have stated that in all the theories mentioned above the water molecules are either assumed to combine with the polar side chains or with the carbonyl group of the protein molecule. They describe a new model. The adsorb-:ed water is assumed to exist in two states, "first water in simple solution and secondly water combined to form hydrate with a defi-:nite unit of the fibre molecule. It is then simply assumed that the three phases of water present in the solid, viz. dissolved water, unhydrated molecules and hydrated molecules - all form an ideal solid solution".

The last of their assumption, viz. the ideality of the solid solution is made, by the authors' own admission, for reasons of mathematical simplification and clearly ignores the physical signi-:ficance involved therein. It is extremely surprising however, that the equation thus derived seems to be the most satisfactory of all the equations. Their heat calculations appear to agree fairly well with Bull's calculations (44). The authors have tested the validity of their isotherm on a number of different experimental data available in the literature and the agreement is so good that their simple model is believed to have some essentially sound features as well as a reality.

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Enough has been said regarding the behaviour of water vapour towards textiles. It is indeed extremely surprising that very little work has been done on the absorption of other vapours by such fibres. Among the few that have thought it worthwhile to explore in other fields, the names of Kanamaru and Chao (50) and Lauter (51) may be mentioned. The former studied cellulose, purified ramie fibres, acetylated ramie fibre, powdered triacetyl cellulose, diacetyl cellulose, di and tri nitro cellulose, etc. As liquids they used: methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, ether, acetone, benzene, acetic acid and chloroform. The results are given in numerous Tables, though the conclusions drawn indicate nothing new. Lauter's work, however, is much more systematic and valuable. His results mainly confirmed the results of Kisau Kanamaru. He showed that the sigmoid shape of the isotherms of hydroxy compounds had something to do with swelling and in those isotherms where the sigmoid shape is not evident (benzene, carbon tetrachloride) the shape of the isotherm is very simple and easy to explain. Unfortunately, Lauter does not appear to have proposed any unified theory to explain the different curves for different liquids on either cellulose or rayon.

King (52 & 53) has published some interesting work on rate measurement for vapours of methyl alcohol, moisture and ethyl alcohol. He points out that diffusion rather than adsorption is

the rate controlling process and the reason for the slowness of diffusion in the case of smaller molecules like water is not so much obstruction ~~afforded~~ offered by the keratin structure as the rather slow ~~diffusion~~ DISSIPATION of the heat generated during absorptions. He gives experimental proof to his theory by measuring the rise in temperature of the textile fibre during absorption. In another paper, the same author (54) has published an account of the effect of strongly hydrogen bonding agents like water and formic acid on nylon and keratin and has shown that the increase in dilectric constant of the adsorbent after adsorption was not dependent on the dipole moment of the adsorbate but was correlated with the decrease in elastic modulus of the adsorbent. This is taken to lend support to the x-ray structures of both nylon and keratin and the view that amorphous nature and elasticity on the one hand and crystallinity and rigidity on the other always go together is regarded as being further strengthened.

ii) EXPERIMENTAL

The data collected include results of rate measurements as well as isotherms. Both sorption from aqueous solution as well as from the vapour phase are studied. Drawn nylon, undrawn nylon and wool are the materials used as sorbents. All the chemicals used were of Analar quality. Acetic acid, methyl alcohol and

ethyl alcohol were all completely dried. The methods of purification are all included in the Appendix. The drawn nylon used was 40 denier but the specification of the undrawn nylon was not known. Both of them were obtained from the same source (I.C.I., Plastics Division.) and it was believed that chemically both were of equal purity. The wool used was sheep wool from which the root ends were specially picked. The scouring of nylon yarn was done in distilled water containing 0.6 g. of Teepol X and 1 c.c. of 0.88 ammonia per litre at 60°C for 20 minutes. The fibre was then thoroughly washed in distilled water and dried in an air oven at 60°C, and conditioned at room temperature for 48 hours and bottled.

The sample of wool was given a very light ammonia scour in the cold and all the adhering dirt was thus washed away. It was squeezed and then rinsed in 95% alcohol, squeezed and dried at 60° in an air oven. It was finally extracted in ETHER IN a Soxhlet apparatus for 24 hours, dried, rinsed in distilled water, dried again, and conditioned and bottled.

Determination of the sorption isotherm or the sorption rate of phenol:-

An exactly weighed quantity of cut nylon (about 1.5 to 2 gm) was put in a conical flask and a calculated amount of phenol solution of a known concentration was poured on to it, the flask

stoppered and placed in a water thermostat at any desired tempera-:ture. For analysis, 10 c.c. of the solution was pipetted out and diluted to a suitable volume and an aliquot portion was removed for titration and analysis. The details of the method are given in Appendix 2.

When isotherms had to be determined, the concentration of the phenol bath was varied but the ratio of weight of nylon to weight of phenol was always kept at 2:1. This point should be particu-:larly noted, because in most cases the material-liquor ratio is kept constant and the material-sorbate ratio is neglected. We did not think that such a procedure was theoretically sound. The volume of liquor taken can hardly be expected to have any influence on the sorption as long as the minimum quantity of liquor taken is enough to wet the fibre completely and allow suitable stirring. The mass of the sorbate however is important, because it may exert an influence on sorption according to the law of mass action.

When rates had to be determined, the sorbate solution taken in all the bottles was the same. But the time of sorption allowed in each case was different.

Benzoic acid and Benzene sulphonic acid

The general procedure for the determination of sorption iso-:therm or sorption rate was similar to that described above, but

the analysis was made by sodium hydroxide solution of 0.01 N strength or 0.1 N strength as required, using phenolphthalein as indicator.

Experimental technique for the measurement of sorption from vapour phase.

In Appendix 2, a detailed account of the technique with a description of the apparatus is given. It is enough to note here that we have used a glass spring of sufficient sensitivity to weigh accurately 0.1 gm of the fibre with an error of $\pm 1\%$. The cleaning of the fibre surface was done by evacuation under high vacuum and over phosphorous pentoxide. The vacuum attained varied from 0.0001 mm to 0.00005 mm. The glass spring was always calibrated at the temperature of the experiment and its length was read by means of a cathetometer reading to 0.001 cm. The evacuation was continued for 4 to 6 hours until a constant weight was registered by the glass spring carrying the fibre sample.

When the sorption was to be determined at the temperature of 25 to 40°C, the sorbate liquid whose vapour was to be studied was maintained at a constant temperature by enclosure in an air thermostat. The sorption tube carrying the glass spiral (see Fig.3d in Appendix 1) was kept in an accurately controlled water thermostat.

When the sorption rates were to be measured at temperatures above 50°C, (as in the case of phenol, acetic acid, B-naphthol

and benzoic acid), the sorption tube and the liquid-bulb were both immersed in a bath containing liquid paraffin, this bath being thermostatically controlled within $\pm 0{\cdot}5^{\circ}C$. A few preliminary experiments with non-absorbing metals showed that the effect of condensation of the sorbate on the fibre due to the small differ-:ence of temperature of the thermostatic bath, was negligible. A figure to show the apparatus used and the details of the experi-:mental procedure are given in Appendix 2.

The adsorbate liquid in all cases was taken in thin sealed glass phials and broken inside the liquid bulb by raising a small piece of iron enclosed in a glasstube by means of a magnet and allowing it to fall over it. The advantages of such a procedure for the introduction of the liquid are pointed out in Appendix 2.

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II

RESULTS AND DISCUSSION

A: SORPTION FROM AQUEOUS SOLUTION

Note: All the tabulated data are included in a separate appendix at the end of the thesis (pp.214-251).

II RESULTS AND DISCUSSION

A : Sorption from Aqueous solution

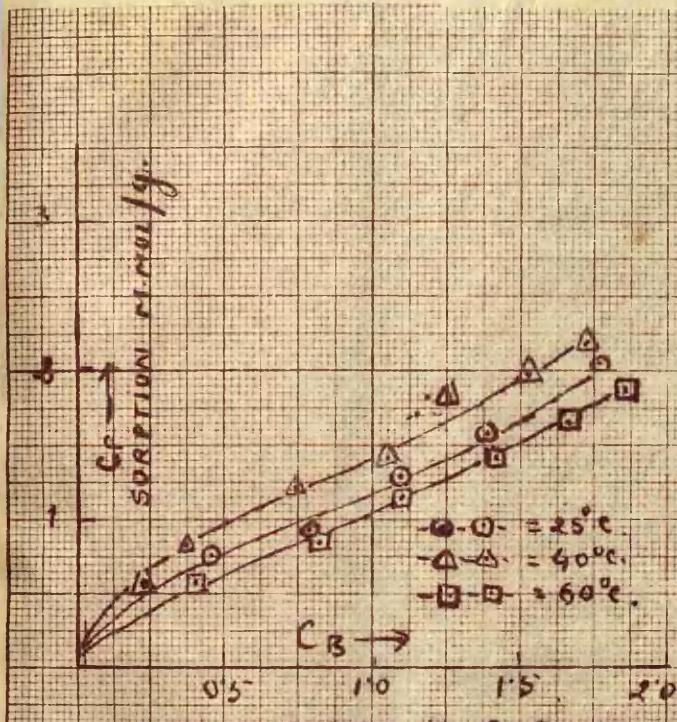
i) Isotherms for phenol on drawn and undrawn nylon.

Tables 1, 2 and 3 give data for the isotherms for drawn nylon at three different temperatures, viz. 25°, 40° and 60°. Tables 4, 5 and 6 give the corresponding data for undrawn nylon. In Figures 1 and 2 are shown isotherms constructed from these data.

(1) It will be noted that in both cases there is no regu-:larity with respect to temperature. Thus the isotherm at 25° takes a middle position with respect to the isotherms at 40° and 60° in drawn nylon whereas the 25° isotherm actually crosses the other two in undrawn nylon. Normally one would expect the three isotherms to lie above or below one another in a regular order. This seems surprising but the explanation is simple.

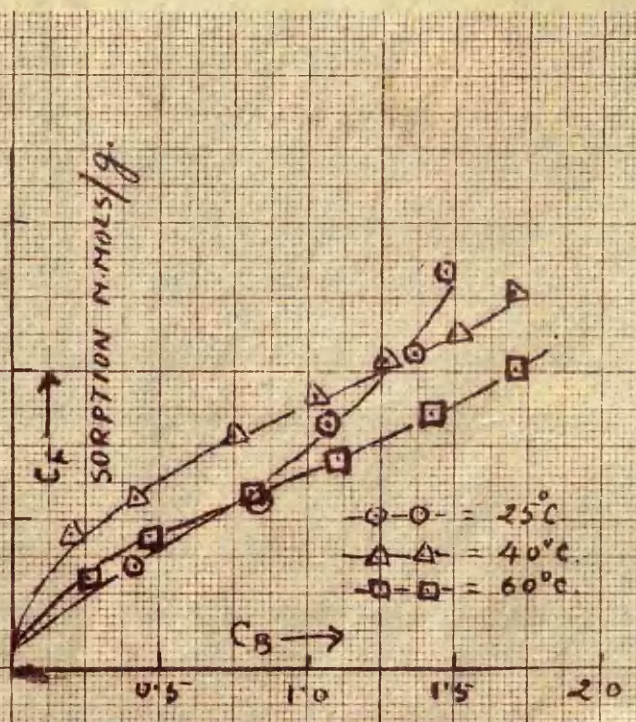
The amount absorbed is not only a function of the concentra-:tion of phenol in the bath but depends also on its solubility in water. The greater the solubility, the lesser the tendency to sorption. The solubility of phenol at different temperatures is known (54A) and this allows us to test if our explanation is cor-:rect. In Figures 3 and 4, the isotherms are redrawn with the values of C_R, the relative concentration of phenol in bath at equilibrium on the x-axis, instead of C_B as in Figures 1 and 2. We define relative concentration as,

$$C_R = \frac{\text{Actual Concentration of phenol in bath } C_B}{\text{Solubility of Phenol in water } S} = \frac{C_B}{S}$$



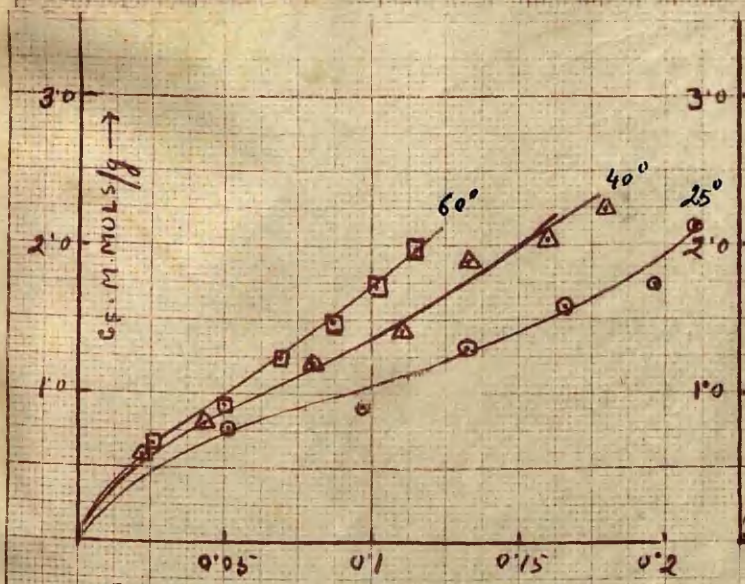
CONC. OF PHENOL IN BATH AT EQUILIBRIUM : g. PER 100 cc.

FIG. 1 : ISOTHERMS FOR AQUEOUS PHENOL ON DRAWN NYLON.



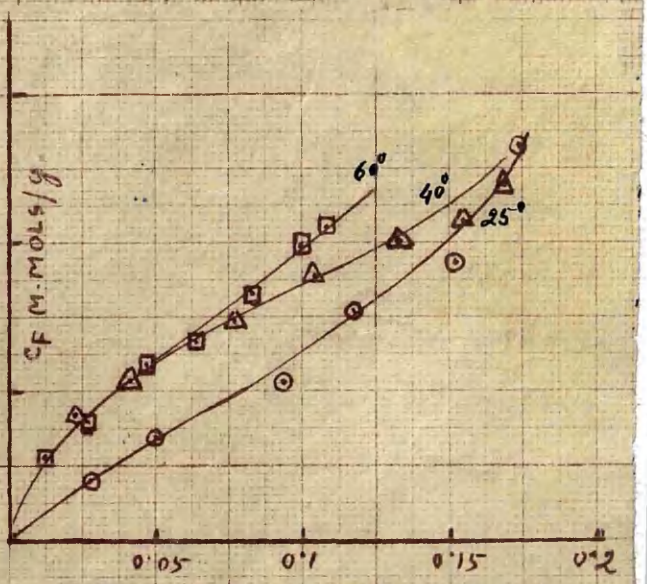
CONC. OF PHENOL IN BATH AT EQUILIBRIUM : g. PER 100 cc.

FIG. 2. : ISOTHERMS FOR AQUEOUS PHENOL ON UNDRAWN NYLON.



RELATIVE CONC. OF PHENOL IN BATH

FIG 3 : SAME AS IN FIG. 1 BUT BATH CONC. EXPRESSED AS REL. CONCENTRATION.



RELATIVE CONC. OF PHENOL IN BATH

FIG. 4 : SAME AS IN FIG. 2, BUT BATH CONC. EXPRESSED AS REL. CONCENTRATION.

Sorption from Aqueous solution.

It is to be noted that the positions of 25° and 40° isotherms show a regularity as expected. But still it is interesting to note that the isotherms at 40° and at 60° more or less coincide with each other. Nevertheless this point of solubility influenc-:ing the course of sorption is extremely important and it is far more reasonable to talk of relative concentration as defined above rather than the actual concentration. This allows us to eliminate the disturbing effect of solubility while studying the effect of temperature on sorption.⊠

(2) A second point of interest is that the isotherms for phenol show a sigmoid shape for both types of nylon at all the temperatures studied. Brunauer (55) classifies the various shapes of isotherms met in the literature into five broad types. Figure 5 shows the different types. Comparing with our isotherms in Figures 3 and 4 the similarity of type 2 isotherm to the phenol isotherms for nylon will be noted. Such isotherms are believed to show multimolecular adsorption (Brunauer, loc.cit.)ϕ

This sigmoid shape is also characteristic of the isotherm for water on various textile fibres. We therefore shall analyse the phenol isotherms in greater detail.

⊠Many of the data for dye-absorption on fibres seem to disre-:gard this point and it is submitted that 'heats of dyeing' calcu-:lated from isotherms at two or more temperatures may not be very reliable.

ϕBrunauer broadened the basis of Langmuir's conception of Uni-molecular adsorption and evolved an isotherm equation which includes both Unimolecular and Multimolecular adsorption.

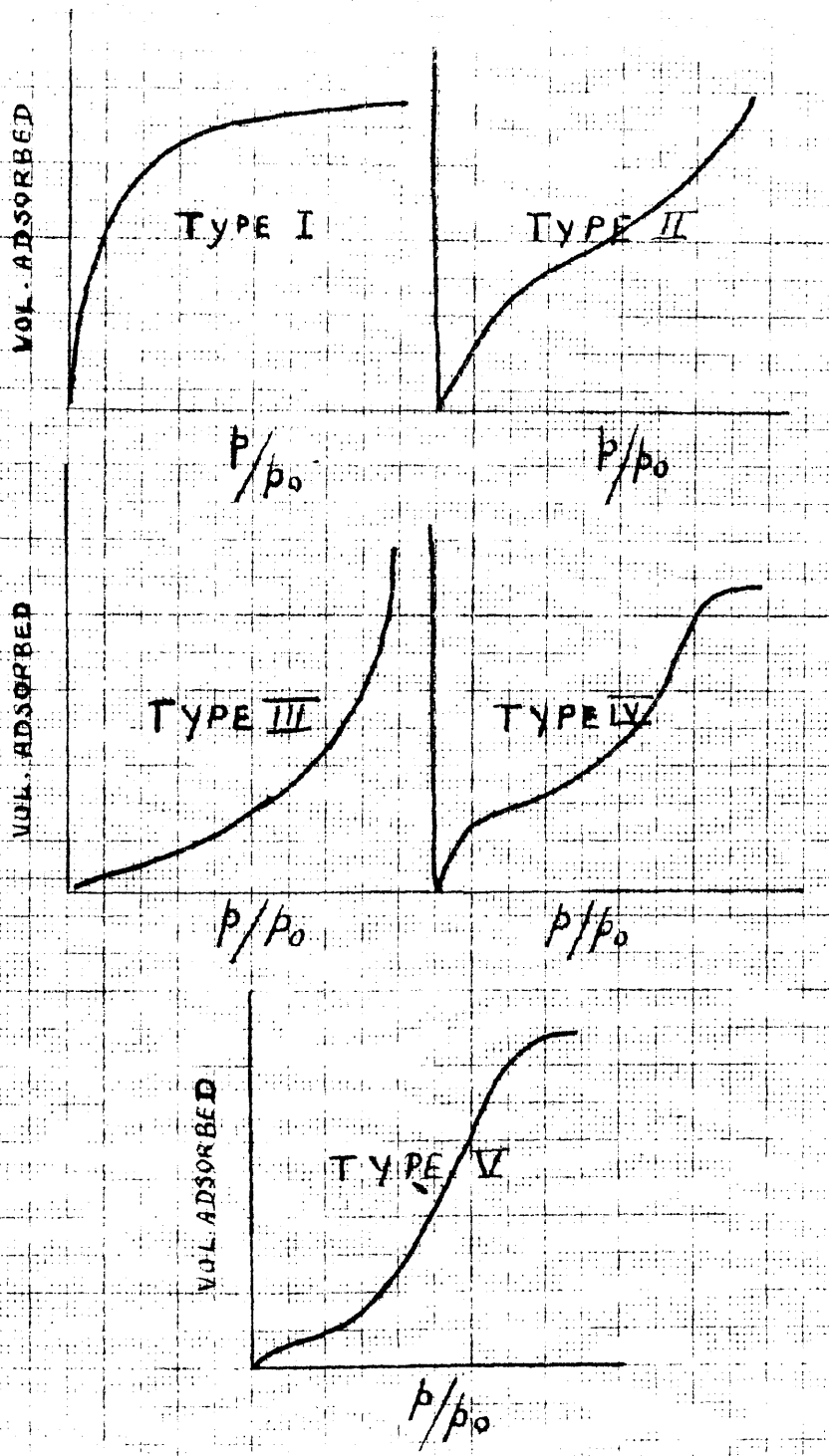


FIG: 5: BRUNAUER'S CLASSIFICATION OF ISOTHERMS FOUND IN LITERATURE

Sorption from Aqueous solution.

In a thesis submitted to the Royal Technical College for the Associateship (56) an equation for the phenol isotherm was derived. The main assumption was that molecules of phenol in solution behave like a gas and that water for all practical purposes behaves as an indifferent medium as far as sorption sites are concerned. Of course such a simple assumption can never be really true in the physical sense. But, it was assumed that water molecules are first taken up by nylon and every molecule of phenol that is absorbed replaces a molecule of water already absorbed, so that the energy change accompanying the sorption of phenol molecules on different sites in nylon was of a uniform nature. The formula derived is given below:-

$$\frac{1}{C_F} = \frac{1}{C_m b} \times \frac{1}{C_B} + \frac{1}{C_m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where

C_F = m. mols of phenol sorbed by 1 g. of nylon

C_B = Percentage (wt/vol.) of phenol in bath at equilibrium

C_m = Amount of phenol necessary to form one complete layer on nylon

and b = a constant.

It was pointed out that equation (1) is exactly similar in form to the Langmuir classical equation.

Skinner and Vickerstaff (25) have derived a similar formula for the isotherms of a few dyes on wool and applied it successfully

to their data. It is however very interesting to observe that the shapes of their isotherms resemble type I (Figure 5) isotherm and not type 2. This would suggest that the surface of wool, in the case of these dyes, showed a constant activity with uniform heat of dyeing.

The shape of our isotherms is definitely sigmoid. And yet when Formula 1 is applied to the data, it is seen that (Figures 6 and 7) the expected straight line relationship is obeyed in both the cases. But there is a very significant feature. Instead of a single straight line, we have two distinct ones, the point of intersection being near 1 m. mol of sorption in all cases. The C_F values read from the graphs are listed below:

Values of C_F at the point of intersection (Figs 6 & 7)

Temperature °C	C_F m.mols/g.	
	Drawn Nylon	Undrawn Nylon
25°	0.833	1.06
40°	0.926	1.14
60°	0.926	1.32

The linear relationship observed in Figs. 6 and 7 and the existence of a breakpoint in the Langmuir curves would indicate that the process of sorption for less than one millimole per gram is uniform, but is essentially different from the process after a sorption of 1 m.mol, though the latter in itself is uniform. In

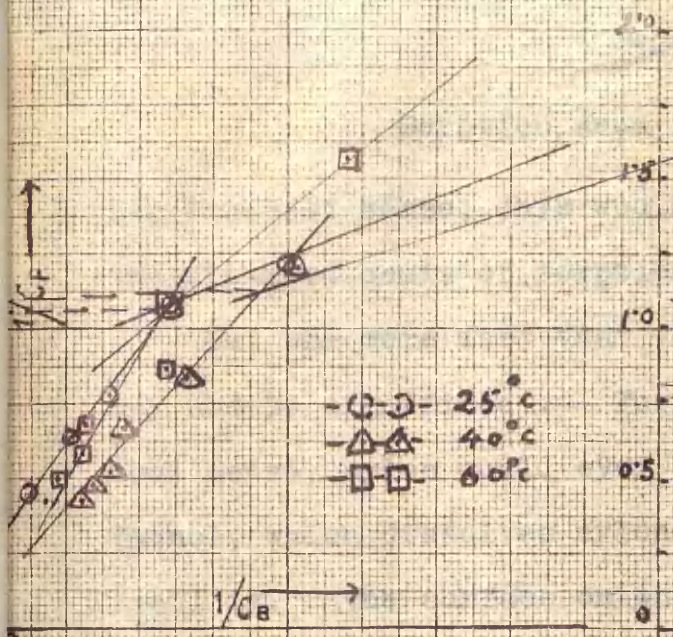


FIG.6 : EQUATION '1' APPLIED TO DATA OF FIG.1 : PHENOL ON NYLON. (DRAWN)

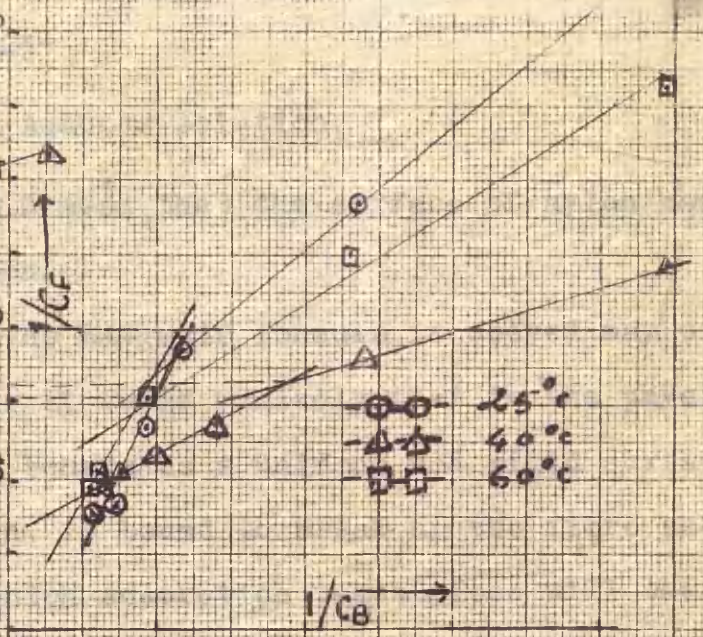


FIG.7 : EQUATION '1' APPLIED TO DATA OF FIG.2 : PHENOL ON NYLON. (UNDRAWN)

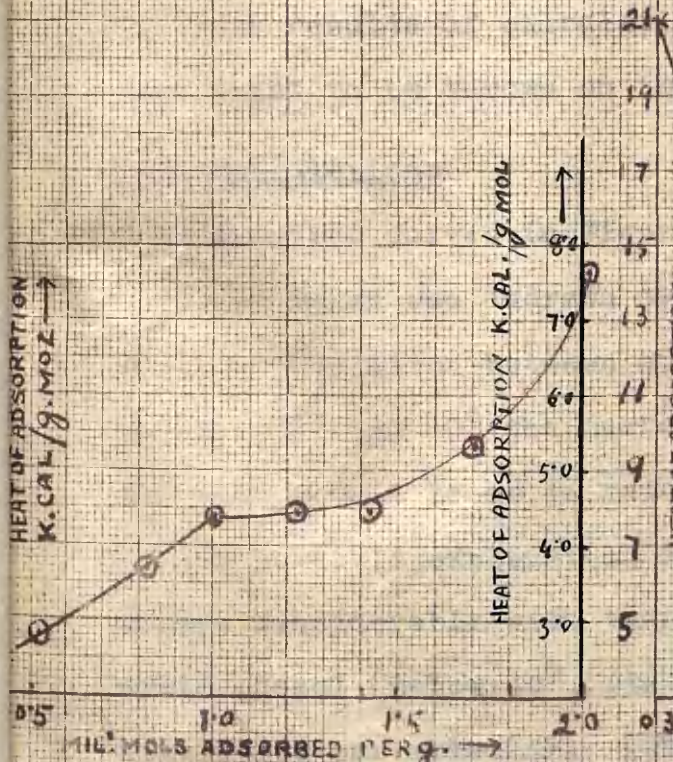


FIG.8 : HEAT OF ADSORPTION FOR AQ. PHENOL ON DRAWN NYLON.

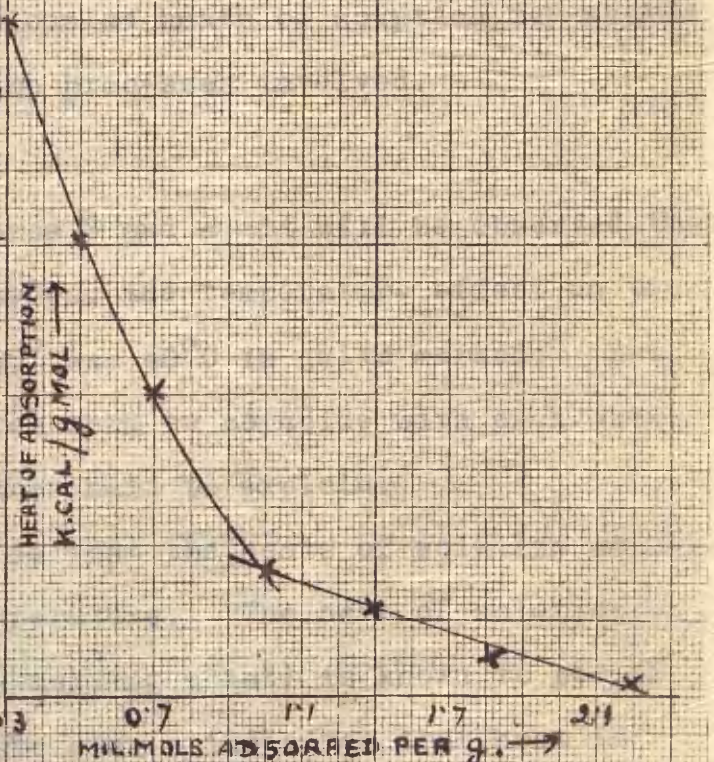


FIG.9 : HEAT OF ADSORPTION FOR AQ. PHENOL ON UNDRAWN NYLON.

its broadest sense, this would mean that the surface of nylon has two distinct heats of sorption.

But the mere fact that the Langmuir formula is obeyed may or may not be significant. For it seems unlikely that in the physi-:cal sense, nylon would ever behave as a uniform and rigid surface. Phenol, which dissolves nylon, is bound to break up the fibre and swell it. The surface on which adsorption takes place will there-:fore increase with the quantity of phenol taken up by the fibre. All that one can conclude from the above is that there are probably two distinct stages in the course of sorption.

The results of calculations of heats of sorption may enable more light to be thrown on the processes involved.

Heat Calculations:

From the curves in Figures 3 and 4, it will be observed that, both for drawn and undrawn nylon, the temperature effect on the course of sorption between 25° and 40°C is quite marked. But between 40° and 60° the curves seem to coincide with each other. Why this should be so is rather hard to explain.

A possible explanation is that the heats of solution of phenol change considerably with temperature. The heat of solution of solid phenol (below 40°, its melting point) is known to be +10 kilojoules per mole (57) (The sign + indicates that heat is

absorbed and not evolved). Its heat of solution above 40° (liquid phenol) does not seem to have been investigated. But we might take the case of acetic acid for indirect evidence. (Acetic acid, like phenol, is a hydrogen bonding agent). The heat of solution of solid acetic acid (58) is +8.9 k.joules per mole. But that of liquid acetic acid is very different. It actually changes sign and becomes equal to -1.67 k.joules per mole at 70° and -1.00 at 23°C. Thus at lower temperatures heat is absorbed and at higher temperatures it is evolved. It is possible that such an abnormality exists also in the case of phenol.

To make the significance of this point clearer, we shall calculate the heats of reaction for phenol on nylon by applying the famous Kirchhoff's equation to our isotherms in Figs. 3 and 4. The equation is so widely used that it is not necessary to go into its derivation here. The equation is

$$\frac{2{\cdot}3.R.T_1.T_2}{(T_2-T_1)} \times \log\frac{C_1}{C_2} = +Q \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where R = gas constant (1.98 cal./mol)

T_1 & T_2 = Temperatures at which the two isotherms are determined,

C_1 & C_2 = Concentration of the equilibrium baths for a given amount of sorbate taken up by the sorbent at the temperatures T_1 and T_2 respectively

and + Q = Heat absorbed in the process.

Sorption from Aqueous solution.

The above equation has been used and heats are calculated from the isotherms at 25° and 40° for both the nylons. The data are given in the following table.

T A B L E 7

Heats of sorption (cal. per mol.) of Phenol on drawn and undrawn Nylon between 25° and 40°

Amount sorbed millimol/gm	0.5	0.8	1.0	1.2	1.4	1.7	2.0
Drawn Nylon	2790	3790	4400	4400	4400	5275	7700
Undrawn Nylon	21,400	15,100	11,200	6,200	5,450	4,250	3,250

From the above data curves are constructed showing the relation between the amount of phenol absorbed and the heat absorbed. These are shown in Figs. 8 and 9.

The heat curves are indeed very remarkable. We note that:-

(1) The heats are positive throughout. In other words the sorption reaction is endothermic.

(ii) Drawn nylon and undrawn nylon show reverse heat effects with increasing sorption. In the former, the heat of reaction increases with increasing sorption. In the latter the reverse is the case.

(iii) The initial heat of reaction is very small for drawn nylon. Thus at 0.5 millimol per/g. sorption it is only 2,700 and for lesser sorption it is even less. For undrawn nylon the ini-:tial heat is very large. Thus for 0.5 millimol sorption 21,400 cals are absorbed.

Points (ii) and (iii) are very interesting and significant. A similar anomaly was reported by Speakman (59) who calculated the heats of sorption for water vapour on drawn and undrawn nylon. He found that at high values of water sorption drawn nylon gives smaller heat values whereas at low water sorption values it gives higher heat values when compared with undrawn nylon. He does not attempt to explain the behaviour.

We offer a tentative explanation for phenol.

Forgetting for the moment all complicating evidence, let us try to picture what might happen when phenol molecules are sorbed by nylon. It is felt that three types of energy changes must be taken into account.

(i) Firstly a quantity of heat q_1 will be absorbed when phenol molecules attach themselves to the "free" carbonyl groups, by hydrogen bonding. The phenol will also probably be attached to the free -NH - groups in nylon. It is likely that the energies of hydrogen bonding between NH...$\overset{H}{O}$-Ph and =CO...HO-Ph are differ-:ent (about 6 k.cal. for O...HO bond and 3 k.cal. for NH...O bond

according to Pauling) but the difference is so small that for the sake of argument we shall assume that these energies are equal,

(ii) It is also likely that phenol molecules will break existing NH...OC bonds in nylon and that there will be a certain amount of heat, say $(-q_2)$, evolved.

(iii) It is well known that phenol swells nylon. Our preliminary observations also showed that drawn nylon suffers severe contraction in length and also probably swells in diameter during sorption. Work has to be done on nylon for this swelling and contraction and so heat must be absorbed. Let us represent this heat by q_w.

Naturally the resultant heat of reaction Q would be given by

$$Q = q_1 + q_w - q_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Now as Figures 8 and 9 show the resultant heat is positive, hence we can infer that

$$q_1 + q_w > q_2$$

Further q_2, the heat required to break the existing bonds in nylon must be the same whether it is drawn nylon or undrawn nylon. This means that the reverse effect observed cannot be attributed to the q_2 being different for drawn and undrawn nylon.

That means an explanation has to be found in the resultant

value of $q_l + q_w$. In drawn nylon, we must infer, $q_l + q_w$ increases with increasing absorption. It will be appreciated that due to a large number of free - CO-and -NH-groups available for bonding in undrawn nylon, q_l is likely to be greater for undrawn than for drawn nylon. On the contrary due to the necessarily greater amount of work done in swelling and contraction, q_w is likely to be greater for drawn nylon than for undrawn nylon. We might therefore say that the initial high heats of absorption for undrawn nylon are due to q_l, being very great - i.e. due to the combination with free - NH-and -CO- groups. As absorption proceeds their number diminishes and so the heat value falls. In the case of drawn nylon the main factor which determines the resultant heat is q_w and the work of swelling and contraction seems to increase gradually as absorption proceeds. In the purely physical sense we might interpret this to mean that due to absorption of phenol molecules on to-NH - CO-groups, the mass to be displaced goes on gradually increasing, and hence the value of q_w goes on increasing.

We might therefore conclude that

(i) In drawn nylon the heat equivalent of the work involved in swelling and contraction increases with increasing sorption whereas the changes in the heats of hydrogen bonding or bond-breaking are comparatively less significant. As a result the

resultant heat increases gradually with sorption.

(ii) In Undrawn Nylon, the initial high heat is due to hydrogen bonding of phenol molecules with the free - CO - or -NH- groups. The value of this falls as the free sites are occupied. The changes in the heats of 'bond-breaking' or heats of swelling are not significant and hence the resultant heats diminish with increasing absorption.

There is yet another point which needs to be explained: what is the exact significance of the point of intersection in the Langmuir curves? Even the heat curves show a break at the same point as shown by the Langmuir curves. The above considerations are enough to show that the details of the energy changes are far too complicated and only a qualitative explanation is possible. Broadly we can say that below 1 millimol per g. sorption, the sorption in drawn nylon consists of breaking up bonds and swelling and contracting the fibre. In the case of undrawn nylon, under 1 millimol per g. absorption, it mainly involves linkages with free Carbonyl and amide groups in the fibre. After 1 millimol per g. the fall in the heat is less gradual with increasing absorption because there are no more free carbonyl groups left in the undrawn fibre. The increase in the heat value under similar conditions is more in drawn nylon, because as the weight of the molecules to be displaced goes on increasing with increasing amounts of phenol, the work done in displacing the molecules requires more heat.

This however is a tentative suggestion and nothing ~~could~~ can be said conclusively until new theories are developed which take into account in a rigorous mathematical fashion all the energy changes involved in the sorption.

RESULTS AND DISCUSSION

II A : Sorption from Aqueous Solution (continued)

(ii) Isotherms for resorcinol, aniline, benzoic acid and benzene sulphonic acid on nylon.

It is clear that the hydroxy group in phenol plays a very important part in its action on nylon. To decide whether the action of the hydroxy group is due to the acidic nature of the phenol molecule, three identical samples of nylon were immersed in 1.68% phenol solution with a material liquor ratio of 1:50, in the following manner.

Solution I = 50 c.c. of Phenol solution + 0.5 c.c. (conc) hydrochloric acid, pH = 2.

Solution II = 50 c.c. of Phenol solution + .65 g of "Analar" sodium hydroxide, pH = 13.

Solution III = No addition of acid or alkali, pH = 6 to 7.

It was found that the alkaline solution showed no absorption whereas the neutral and acidic solutions gave sorptions of 13.61% and 14.98% respectively. The effect of acid in determining absorption was therefore regarded as very slight. The fact that alkaline solution of phenol shows no absorption at all was a decisive proof for the correctness of the assumption that the hydrogen atom of the phenol molecule was directly involved in binding.

It has long been known that weak organic acids such as

acetic, formic or chloracetic acid, have all an abnormally high sorption on wool. This fact has been variously explained by different workers. But the general opinion follows Speakman's theory. Speakman and Scott (12) investigated the action of strong acids as well as weak acids and concluded that the weak acids enter the micelles of wool and swell the fibre and expose a greater surface for absorption. This must be the reason for higher absorption. Oxalic acid was found to behave as a mono basic acid.

It was felt that it was very probable that the combination of weak organic acids and protein may not be ionic at all. Most of the organic carbonxilic acids are strongly hydrogen bonding in nature and this might play a decisive part in their action on the peptide molecules. It was therefore decided to study the isotherms of resorcinol, aniline and benzoic acid on nylon. In the case of resorcinol and aniline, both drawn and undrawn nylon were studied. With benzoic acid only drawn nylon was used.

Experimental procedure: The same samples of nylon as were used in Section I were employed. As in the case of phenol, the material-sorbate ratio was kept constant and the volume and concentration of the sorbate solution were varied. The method of analysis of resorcinol and aniline was exactly the same as for phenol. Benzoic acid was analysed by .01 N sodium hydroxide.

Sorption from Aqueous solution

All sorptions were done at 25°C in a thermostat.

The results, as in the case of phenol are expressed in millimol per g. for the amount of sorption and in relative concentration for the equilibrium concentration.

Tables 10, 11, 12, 13 and 14 show the experimental results. Figs. 10, 11, 12 and 13 show the isotherms constructed from these data. We shall discuss each of these compounds separately.

Resorcinol: In Fig. 10, curves are shown for the isotherms - for resorcinol on undrawn nylon, and drawn nylon.

We note:-

(i) At low relative concentrations (below 0.06), undrawn nylon takes a far greater quantity of resorcinol than does drawn nylon, whereas at higher concentrations the two curves merge into one another. In Fig. 12, are two isotherms for phenol on drawn and undrawn nylon for comparison. It will be noted that the action of phenol is strikingly different: at low relative concentrations, both types of nylon take equal quantities of phenol, but above 0.06 to 0.07 , the undrawn nylon shows higher sorptions as compared to the drawn one. Moreover the entrance of another hydroxyl substituent in the benzene ring, as in resorcinol, increases the acidity (Ka) and melting point, as well as solubility (S) . For comparison these properties are

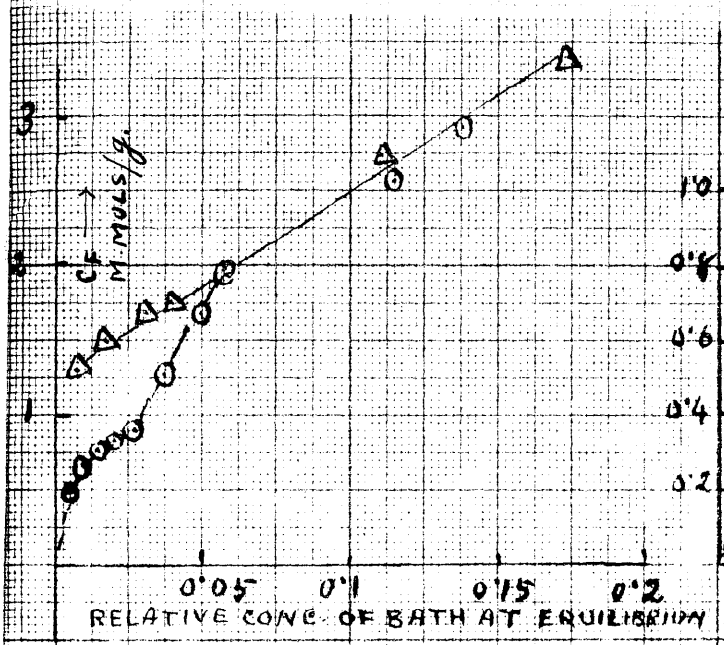


FIG. 10: ISOTHERMS FOR AQUEOUS RESORCINOL ON DRAWN AND UNDRAWN NYLON AT 25°C.

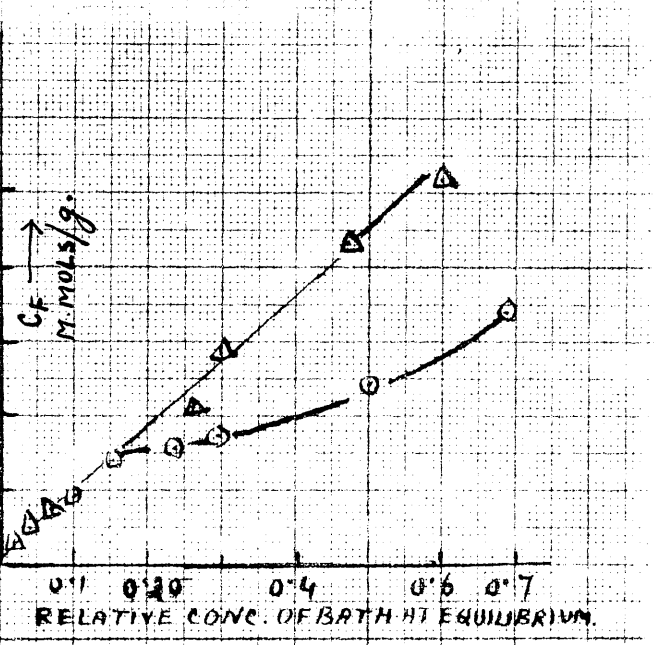


FIG. 11: ISOTHERMS FOR AQUEOUS ANILINE ON DRAWN AND UNDRAWN NYLON AT 25°C.

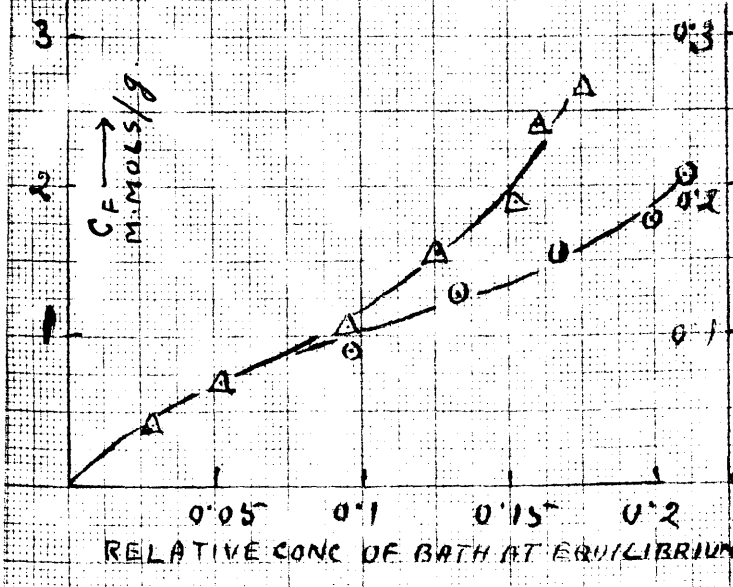


FIG. 12: COMPARISON OF ISOTHERMS OF AQUEOUS PHENOL ON DRAWN AND UNDRAWN NYLON AT 25°C.

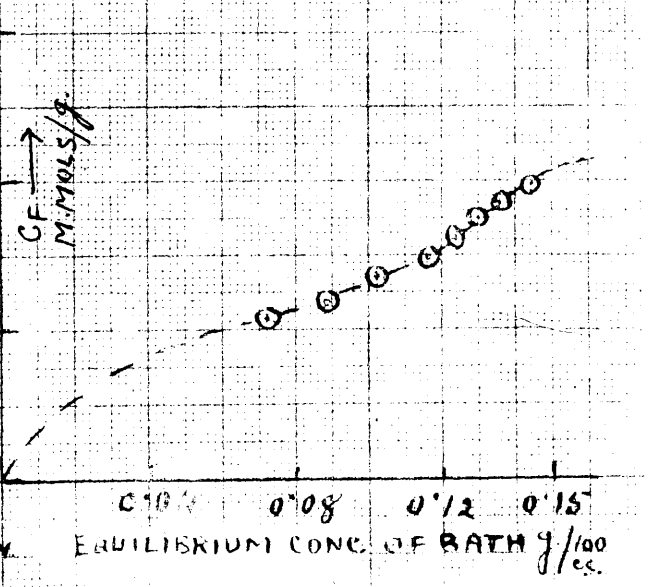


FIG. 12a. ISOTHERM FOR AQUEOUS BENZOIC ACID ON DRAWN NYLON AT 25°C.

Sorption from Aqueous solution

listed below for phenol and resorcinol.

		Phenol	Resorcinol
m.p.	:	$43^{o}C$	$110^{o}C$
B.p	:	$181^{o}C$	$281^{o}C$
$Ka^{25^{o}}$	:	1×10^{-10}	4×10^{-10}
$S^{25^{o}}$	:	8.52 $^{g}/_{100^{c.c.}}$	67.0 $^{g}/_{100^{c.c.}}$

In all these properties, resorcinol shows a much greater tendency towards association and also a greater reactivity. For the same relative concentration therefore it shows a greater sorp-:tion on both drawn and undrawn nylon. The actual mode of com-:bination is presumably by hydrogen bonding, but the strength of binding must be assumed to be greater in the case of resorcinol than in the case of phenol. The affinity of resorcinol towards nylon must therefore be assumed to be greater than that of phenol.

(2) A second interesting point is that in the case of <u>un-:drawn</u> nylon, the quantity of resorcinol taken up reaches a value of about 1.2 millimol. per gm. even at as low a relative concen-:tration as 0.002. After this point, the sorption isotherm is linear, indicating that resorcinol is equally partitioned between the fibre and water. In the case of <u>drawn</u> nylon however such is not the case. There is a distinct break at 0.09 millimol per g. of sorption and the linearity appears only after a sorption of about 2 millimol (see Figure 10). In this case the characteris-

tic sigmoid shape of the isotherm is absent. It would be too much to speculate on the nature of binding between resorcinol only on the basis of a single isotherm. But the break point again at 1 millimol per gm. of sorption may be significant.

Aniline: From the data of Tables 12 and 13, isotherms for absorption of aniline on both types of nylon were constructed (Fig.10). It was very interesting to observe here also a straight line isotherm for undrawn nylon and a sigmoid isotherm for drawn nylon. Unlike resorcinol, there is no distinct break in the isotherm at 1 millimol. absorption. Unlike resorcinol also, at high relative concentrations undrawn nylon shows a far greater sorption than drawn nylon. But the amount of aniline taken up is very small. Thus whereas in resorcinol more than 3 millimol. per gm. are sorbed even at as low a relative concentration as 0.175, undrawn nylon takes up only 1 millimol. aniline and the drawn fibre only 0.6 millimol. even at as high a relative concentration as 0.75.

Equation I (p. 22) was applied to the data for aniline as well as resorcinol. (Figures not shown). Drawn nylon in both cases shows two straight lines. The break in aniline occurs at about 0.29 millimol. per gm. whereas that in resorcinol occurs at about 1 millimol. per gm. sorption. This is the same as in the case of phenol.

Sorption from Aqueous solution

The only inference of any value that can be drawn from the isotherms seems to be that the energy of binding of aniline for nylon is far smaller than that of phenol. Resorcinol, however, has a greater energy of binding. We may conclude that in all cases, the attachment of the molecules is by hydrogen bonding. The sorption of aniline on nylon has also been studied from the vapour phase. We shall have occasion to refer to this point again while discussing the results. (p.113).

Benzoic Acid and Benzene Sulphonic Acid Isotherms on Drawn Nylon.

These two acids were chosen with a view to discovering the effect of acid strength on sorption. Of these, benzoic acid is weaker in acid strength but shows a certain hydrogen bonding tendency. The energy of the OH....O bond formed in benzoic acid is inferred to be 4.3 k.cal. per mol. (60). If the attack of benzoic acid was due to acid strength rather than due to hydrogen bonding, one would not expect any great sorption from aqueous solutions. On the other hand, if the combination was due to hydrogen bonding, it should show some comparable absorption with phenol or resorcinol.

It proved rather difficult to study benzoic acid from aqueous solution, because the solubility of this acid in water is very low (0.29 g. per 100 c.c. at 25°C) and hence sorptions of more than

0.25 millimol per gm. could not be obtained. On the other hand, due to the dilution of the solution, analysis became much more accurate and the isotherm could be better analysed with respect to the surface-property of the nylon fibre.

In Figure 12A, the isotherm for benzoic acid is shown. The concentration of equilibrium bath is expressed as C_B and the sorp-:tion as C_F. The sigmoid shape of the graph is worth noting. The top portion of the curve shows a tendency towards reaching a limitting value. Unfortunately values of concentrations higher than 0.15% could not be investigated due to low solubility of ben-:zoic acid.

Even so, that as much as 2.5%, or about 0.2 millimol per gm. could be sorbed by nylon from such weak solutions is remarkable.

Fig. 13 shows the Langmuir curve constructed from the above isotherm. We note again that the Langmuir relation is obeyed for values of C_F higher than about 0.14 millimol per gm. sorption. If the combination of benzoic acid was only with the amino groups in nylon, we should not have expected a sorption of more than 0.036 millimol per gm. (For the number of free amino groups in nylon is known to be .036 to .040).(26). The fact that very much greater amounts of benzoic acid can be taken up by nylon even at such low concentration suggests that the combination of the acid does certainly not involve salt formation at the amino groups

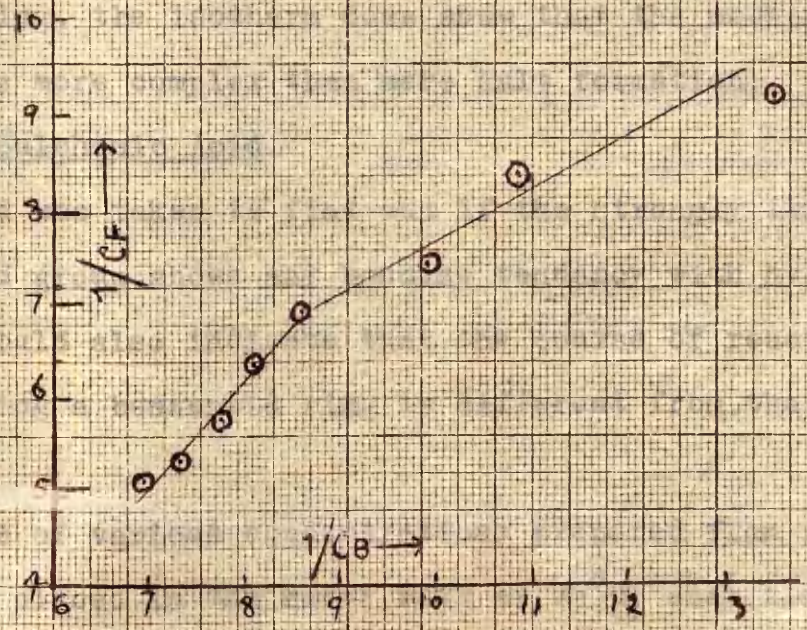


FIG. 13. LANGMUIR ISOTHERM FOR BENZOIC ACID ON DRAWN NYLON AT 25°C.

Sorption from Aqueous solution

It is also noted from the Langmuir curve for benzoic acid, that at a value of $1/C_F = 6.9$ or $C_F = 0.145$, there is a break point. We cannot, however, attach any great significance to this; for it can not be the point of complete combination with the NH_2 groups because they are present only to the extent of 0.036 millimol per gm. It is however likely that this repre-:sents the combination of the benzoic acid molecules with the free carbonyl and amido groups.

Summarising, the isotherm does show that the mechanism of combination is more complex than mere salt formation.

Benzene Sulphonic Acid.

This acid was taken to find out if the strongly ionising sulphonic acid group shows any bonding tendency with nylon. If it does, it would also indicate that the course of reaction with acids containing a benzenoid ring is different from that of min-:eral acids.

Solutions of various concentrations prepared from a 32% w/v solution were placed in the water bath at 25°C, each solution containing the requisite amount of benzene sulphonic acid to make the ratio of wt. of nylon: wt. of acid = 2:1. The amount of benzene sulphonic acid was estimated by titrating 1 c.c. of the solution with 0.1 N sodium hydroxide solution from a microburette, using phenolphthalein as an indicator. The fibre was immersed in the acid solution for 48 hrs. and yet no trace of any absorp-

:tion occurred. Various concentrations of benzene sulphonic acid ranging from 0.1% to 2.5% were used.

This result was interesting. Boulton (27) has reported figures for sorption of this acid by nylon and he found sorptions ranging from 0.013 to 1 millimol/gm. from solutions ranging from 1.89 to 0.24 pH. Experiments were repeated using the pH range reported by him and still no trace of absorption could be detect-:ed.

One thing seems to be clear; the activity of benzene sul-:phonic acid towards nylon is much less than benzoic acid and pro-:bably than other weak acids or phenols. We infer that in the case of organic hydroxylic or carboxylic compounds the binding is more due to hydrogen bonding than due to ionic combination.

RESULTS AND DISCUSSION

II A : Sorption from Aqueous Solution (continued)

(iii) Studies on Rates of Sorption of Phenol and Benzoic Acid from Aqueous Solution on Nylon

By studying the isotherms of phenol and benzoic acid we came to the conclusion that the equilibrium condition for sorp-:tion was determined by a set of contending heats of reactions. There are positive heat values for the work of swelling, contrac-:tion and for hydrogen bonding with the -NH- and -CO- groups of nylon on the one hand and negative heat values for the disruption of hydrogen bonds. An interpretation of the isotherms on the basis of pure classical theories is therefore likely to mislead us. The successful application of Langmuir's "condensation-evaporation" mechanism (in our case "sorption-desorption") might indicate the existence of a resultant uniform heat of reaction, but this is insufficient to prove that at all points of the Langmuir straight-line, all the sorption sites would show an iden-:tical heat of reaction. Other energy changes might take place and the net heat of reaction might just be enough to give a straight line in the Langmuir curve. We also indicated that the non-rigidity of the sorbent surface was the basis of at least some anomalies. It was decided to take up the study of the rates of sorption for phenol and benzoic acid to see if the above inference would be justified.

Experimental Procedure.

Sorption from Aqueous solution

Experimental Procedure

The procedure was similar to that used for the determination of the isotherms (see p.33). Both drawn and undrawn nylon were studied.

Phenol

Rates of sorption from aqueous phenol solutions of three different concentrations, viz. 2%, 2.5% and 3% were studied. For each concentration, three different temperatures were tried,(25°, 40° and 60°C). In all cases temperatures were thermostatically controlled within ±0.25°C. Both drawn and undrawn nylon were studied.

In Tables 15, 16 and 17, rate data for drawn nylon are included In Tables 18, 19 and 20 the corresponding data for undrawn nylon are included.

In Figs. 14, 15 and 16, curves are drawn for the amounts sorbed vs. time (drawn nylon). Curves in Figs. 17, 18 and 19 show corresponding rates for undrawn nylon. It is to be noted that -

(i) The initial portion of all the curves show a regularity with respect to the effect of temperature on the rate. The higher the temperature, the greater the rate. This is quite understandable; because with increasing temperature the activity of the phenol molecules increases, due to increased thermal agitation.

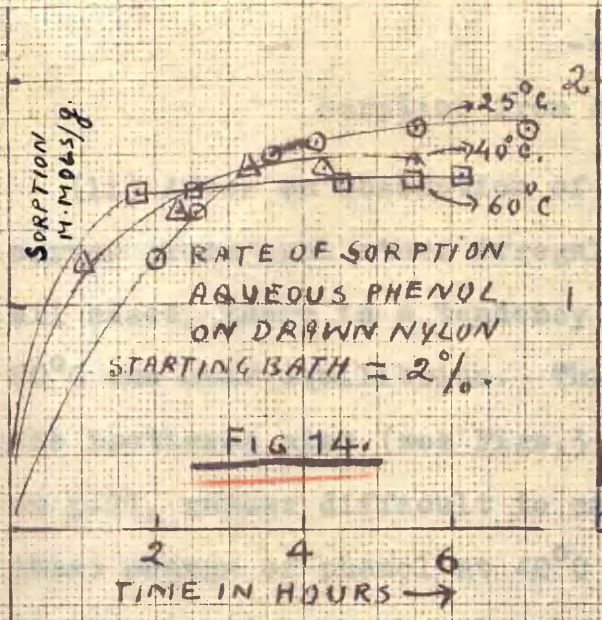


FIG 14.

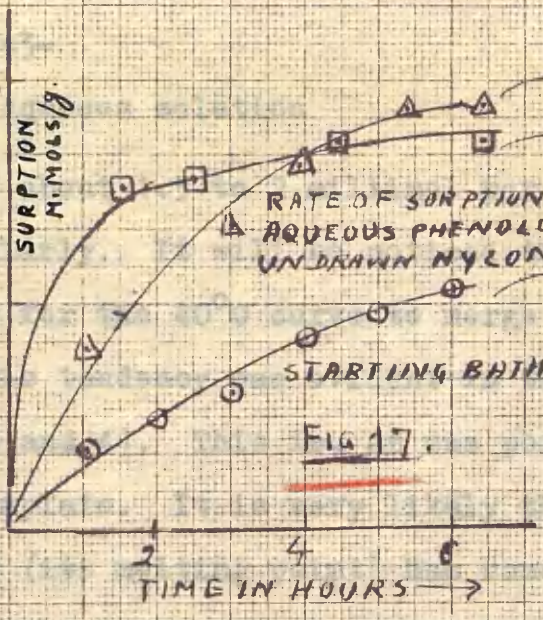


FIG 17.

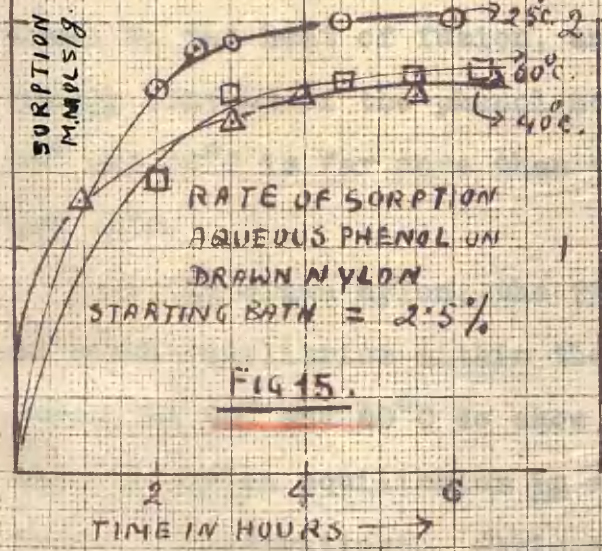


FIG 15.

FIG 18.

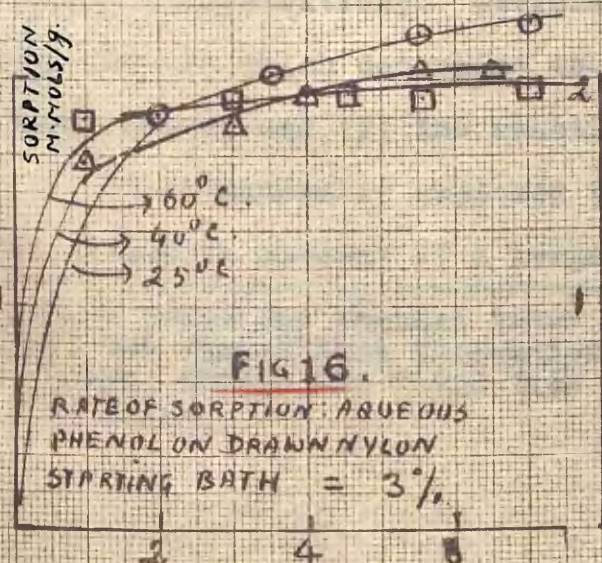


FIG 16.
RATE OF SORPTION: AQUEOUS PHENOL ON DRAWN NYLON
STARTING BATH = 3%.

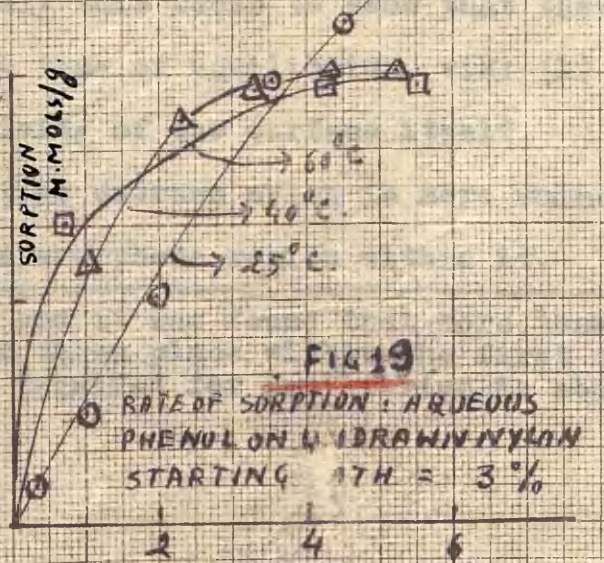


FIG 19.
RATE OF SORPTION: AQUEOUS PHENOL ON UNDRAWN NYLON
STARTING BATH = 3%

(ii) After an absorption of about 1.5 to 2 millimol per gm. the curves cross each other irregularly. It will be noticed that, in all cases, there is a tendency for the 40°C curve to merge into the 60°C one near equilibrium. This tendency was evident in the case of the isotherms also (see Figs.3 and 4). This is, as was pointed out on p.21, rather difficult to explain. It is very likely that the phase change of phenol at 40°C (its melting point) has some influence At this point each phenol molecule increases in energy by an amount equal to the heat of fusion, and it is likely that the increase in energy content of the phenol molecule between the temperatures of 25° and 40°C is far more than that between the temperatures of 40°C and 60°C.

(iii) In drawn nylon, the 25°C curve does not show any tendency to reach equilibrium within the first six hours or so,§ whereas the curves at 40° and 60°C do show such a tendency. Quite remarkably, in drawn nylon equilibrium <u>is</u> attained for all the temperatures and at all concentrations. Obviously this seems to show that there are two factors which determine the time of equilibrium, viz: (1) the temperature, and (2) the reactivity of the surface itself.

It is generally supposed that undrawn nylon is more vulnerable to attack on account of a large amorphous region within it.

---

§ This point was checked later and it was found that more than 90% of the equilibrium absorption takes place within the first six hours, though the total time required for equilibrium is about 24 hours.

One would therefore expect that the undrawn nylon would show a higher initial rate of reaction than drawn nylon. Comparison of the curves in Figs. 14 and 17, 15 and 18, and 16 and 19, shows that this anticipation is not correct. In fact the rates at 25°C show an exactly reverse effect. In the following Table are given the amounts of phenol absorbed at different initial intervals of time for drawn as well as undrawn nylon at the three concentrations studied.

TABLE 21.

Comparison of initial rates of absorption from Aqueous phenol solutions on Drawn and Undrawn Nylon

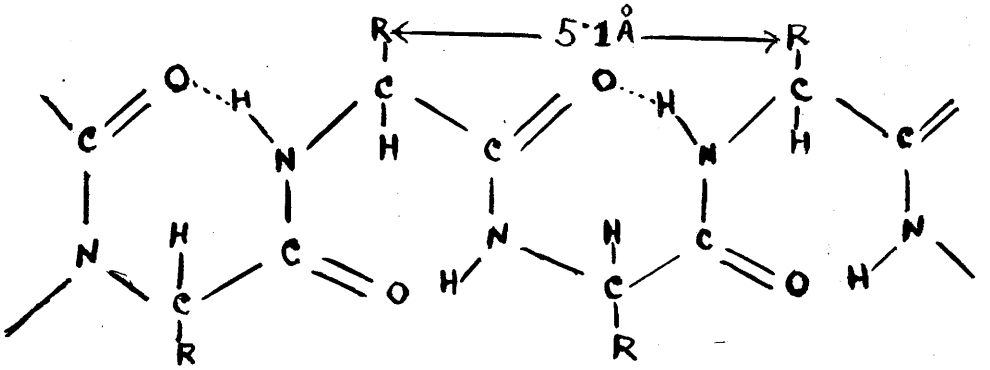
	Amount sorbed millimol/gm.		
Bath conc.	Time (hr.)	Drawn Nylon	Undrawn Nylon
2% Phenol	1	0.73	0.33
	2	1.20	0.50
	3	1.53	0.66
2.5% Phenol	1	1.38	0.50
	2	1.72	0.83
	3	1.93	1.06
3% Phenol	1	1.5	0.50
	2	1.83	1.00
	3	2.00	1.57

It will thus be seen that, particularly at 25°C, the initial rate of absorption for drawn nylon is greater than that for undrawn nylon. It is possible to suggest as an explanation that the rate

of reaction depends more on the available surface area rather than on the extent of the amorphous region. Drawn nylon, is made by stretching the undrawn material $3\frac{1}{2}$ to 4 times its original length. Hence the surface available for absorption in this case is far more than in the case of undrawn nylon.

It would perhaps be a mistake to conclude from this emphatically that there is no such thing as a more reactive amorphous region. But the point raised is one which, it is felt, still needs further clarification. Our knowledge of the actual configuration of the molecules in the amorphous regions of textile fibres is by no means satisfactory. Very recently Bamford and Hanby have published (61) very interesting evidence for the α-protein structure in the case of synthetic polypeptides. They report that they have studied various synthetic polypeptides and invariably the repeat unit shows a length of 5.1 Å. Stretching of the synthetic fibre does not make any difference in the length of the repeat chain, as in the case of wool: (the repeat distance in unstretched wool-keratin is 10.2 A^{O} whereas that in stretched wool-keratin is 5.1 A^{O}). Bamford and Hanby suggest that it is no longer necessary to visualise the various cross linkages to explain the elastic properties. They suggest a "coiled" structure

for the polypeptide molecule of the following type:-



These investigators found no evidence of any β-structure in the synthetic polypeptide polymers. Further, a wooden model of the peptide molecule constructed on the above idea of "Coiled Chains" (62) is reported to show extreme flexibility and mechani-:cal advantage. In consequence Bamford and Hanby suggest that the phenomenon of stretching can be explained by assuming that chains constituted as above can slip past one another without in-:volving any breaking of existing bonds or formation of any new ones. (It will be recalled that on p. 29 , we explained the in-:crease in the heat of reaction in drawn nylon as caused by an increase in the work of swelling and contraction. If Bamford and Hanby's suggestion is accepted, the increase in work could simply be explained as the increase involving contraction of the heavier phenol bonded molecular chains).

To return to our rate curves for phenol, it will be appreciat-:ed that the study of the temperature variation of the rates of

Sorption from Aqueous solution

phenol-sorption on nylon is in its very nature complex. Even so, we shall attempt to examine our experimental data from the point of view of the fundamentals of the kinetics of rate processes.

According to Langmuir, the experimentally measured rate is the difference between the rate at which molecules 'condense' on the surface and the rate at which they leave the surface. If the rate is determined at constant pressure, it is given by

$$\frac{d\theta}{dt} = K_1 (1 - \theta) - K_2\theta \quad \text{.....(4)}$$

where θ is the fraction of surface covered with the sorbate and K_1 and K_2 are constants. Integrating with the boundary condition that $\theta = 0$ when $t = 0$, we obtain

$$\theta = \frac{K_1}{K_1 + K_2} \left\{ 1 - e^{-(K_1 + K_2)t} \right\} \quad \text{.....(5)}$$

when $t = \infty$, $\theta = \theta_e$ = the equilibrium value for sorption.

This gives the relation

$$\theta_e = \frac{K_1}{K_1 + K_2} \quad \text{.....(6)}$$

Now θ represents the fraction of the surface covered by the adsorbate molecules at any instant and θ_e is that when the equili-

:brium quantity is adsorbed. Let C_e represent the amount of adsorbate taken up by the fibre at equilibrium and C_F the amount taken up at any instant. Let C_m be the amount necessary to cover the entire surface by a unimolecular layer. Then obviously

$$\theta = \frac{C_F}{C_m} \quad \text{and} \quad \theta_e = \frac{C_e}{C_m} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Substituting in equation (5), we obtain,

$$C_F = C_e\,(1 - e^{-kt}) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Where $K = K_1 + K_2$

$$\text{or} \quad L_n \frac{C_e}{C_e - C_F} = Kt \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Equation (9) is in a form which can be readily tested. A plot of $L_n \frac{C_e}{C_e - C_F}$ against t should give a straight line and the value of the slope should give the constant K, which in fact would be the sum of K_1, the velocity constant of the forward reaction, i.e. adsorption and K_2, the velocity constant of the reverse re-:action, i.e. desorption.

Equation (9) has been applied to the data of the rates of ab-:sorption of aqueous phenol on nylon. Figs. 20, 21 and 22 show the curves for <u>undrawn</u> nylon for the three temperatures indicated. Figs. 23, 24 and 25 show the corresponding curves for <u>drawn</u> nylon.

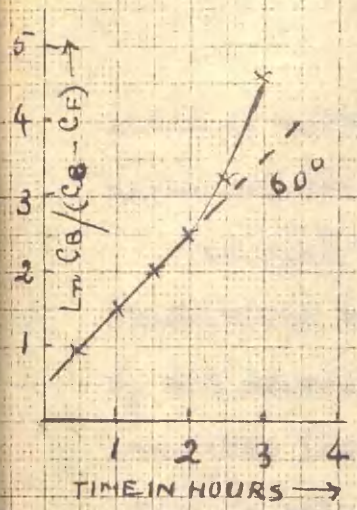


FIG 20.

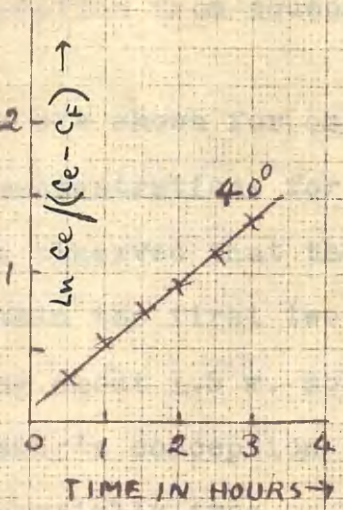


FIG. 21.

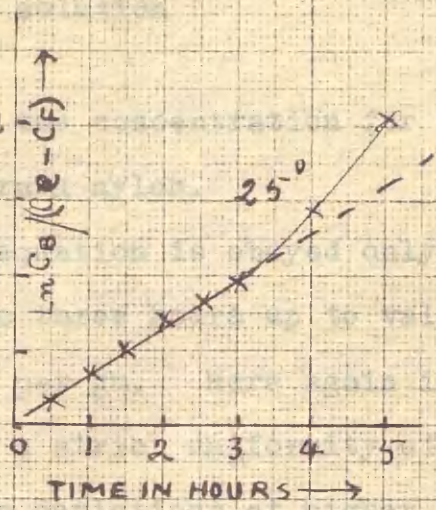


FIG. 22.

AQ. PHENOL ON UNDRAWN NYLON

APPLICATION OF LANGMUIR RATE EQUATION

AQ. PHENOL ON DRAWN NYLON

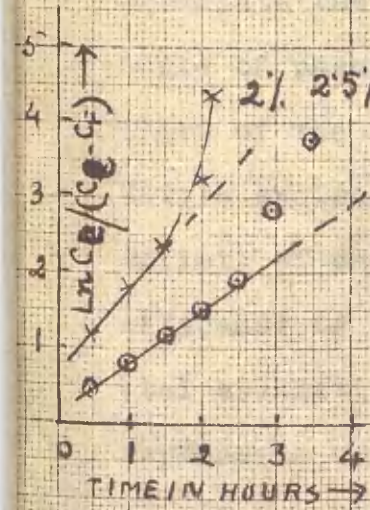


FIG. 23.

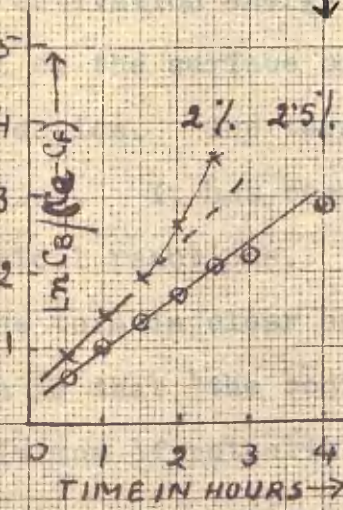


FIG. 24.

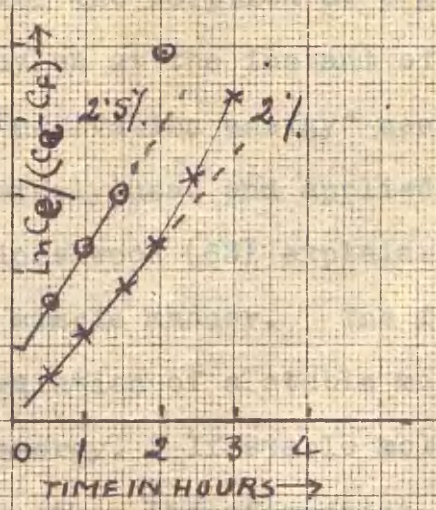


FIG. 25.

Sorption from Aqueous solution

Actually curves are shown for only one concentration for undrawn nylon and two concentrations for drawn nylon.

It will be observed that the equation is obeyed only for absorptions within the first two to three hours up to values of C_F not exceeding about 1.5 m. mol. per gm. Here again it will be seen that Langmuir's conception of a strict uniformity of the surface is only partially true. The deviations at higher sorptions are a clear proof of this. No useful purpose would therefore be served by analysing the curves further or by trying to ascertain the exact significance of the fact that the values of the constant K in equation (9) change with increasing absorption after a time.

We could however utilise the curves in Figs. 14 to 19, to calculate the "activation energy" for the sorption of a gram molecule of phenol on the surface of nylon at the instant of the start of the reaction. The term "activation energy" needs a little explanation. It has been widely used and applied to a variety of chemical reactions. Hinselwood (63) explains the significance of the term in clear and simple manner. The fundamental assumption is that "the configuration of a stable molecule represents a minimum of potential energy. If stable molecules rearrange themselves by chemical or other transformation, the new state also represents a minimum of potential energy. There must

be intermediate states where the potential energy is greater than the initial or the final states. Somewhere in the intermediate region there must be a maximum which may be likened to a pass over which the molecules must travel in the course of the reaction..... The energy which must be supplied to the reacting substances to make them capable of chemical transformation in to the products, is called the activation energy.

It is thus to be noted that activation energy and the heat of reaction are not the same. The heat of a reaction is the measure of the actual energy change between two molecules as a result of the reaction. The activation energy is the surplus energy which molecules must possess to make a reaction possible. In fact the heat of reaction is the difference of the activation energies of the direct and reverse reactions.

We revert again to the specific case of absorption of phenol on nylon. It would be useful to find out the activation energy for this process. We can approach this problem in two ways. We could derive an equation which will satisfy the data of Figures 14 to 19, to fit all or each of the curves, and from the equation calculate the value of the velocity constant of the adsorption reaction for each temperature. We can then apply the Arrhenius equation and calculate the energy of activation. The derivation

of the Arrhenius equation is given by Hinselwood (loc.cit. p. 41-42) and we shall only assume it here. The energy of activa-:tion so calculated would be the average energy for the entire rate of reaction.

Alternately, we can calculate the velocity coefficient only at the zero point in the rate curve and then apply the Arrhenius equation and calculate the energy of activation only at the zero point. We propose to follow the second alternative, because it is difficult to find a single equation which could fit all the rate curves. An attempt was made to fit an empirical formula used by Vickerstaff to calculate the energy of activation for a number of dispersed dyes on nylon (25). It was found, however, that this author's simplified formula for the hyperbolic function does not fit our results. Secondly, even if we succeeded in getting an average energy of activation, its value would be diffi-:cult to assess on account of the inherent complexity of the adsorption mechanism as evidenced by our study of the isotherms.

The calculation of the zero point activation energy however will represent the absolute energy of activation for the adsorp-:tion of phenol on nylon. If the process is essentially one of hydrogen bond formation between -NH-CO- groups and the phenol mole-:cule, the zero point energy for both drawn and undrawn nylon

would be the same. If on the other hand the process of adsorp-:tion in the types of fibre is essentially different, the values of the activation energies would be significantly different.

The Arrhenius equation may be written - (~~Bre n.~~).

$$\frac{d \ln K}{dt} = \frac{A}{RT^2} \quad \text{.....(1o)}$$

Where K = the velocity constant for any reaction,

A = the activation energy,

R = the gas constant and

T = the absolute temperature at which the reaction is carried out and

t = the time.

It follows from equation (10) that

$$\ln K = C - \frac{A}{RT}$$ where C is a constant

A plot of ln K against I/T should give a straight line, the slope of which gives the value of A/R. If R is taken as 1.98 cal., then A is measured in cal. per gm. mole.

The solubility change of phenol with varying temperature is an important factor, however, and we must therefore make an appro-:priate correction.

Let c be the concentration of phenol in solution at a given temperature and S be its solubility in water at the same tempera-:ture.. It is obvious that the rate of sorption is directly

proportional to c and inversely proportional to S. It would also be directly proportional to the absolute temperature, T. Then if X is the amount adsorbed at a time t, the volocity constant K would be given by

$$\frac{dx}{dt} = K \cdot \frac{C}{S} T \quad \ldots\ldots\ldots\

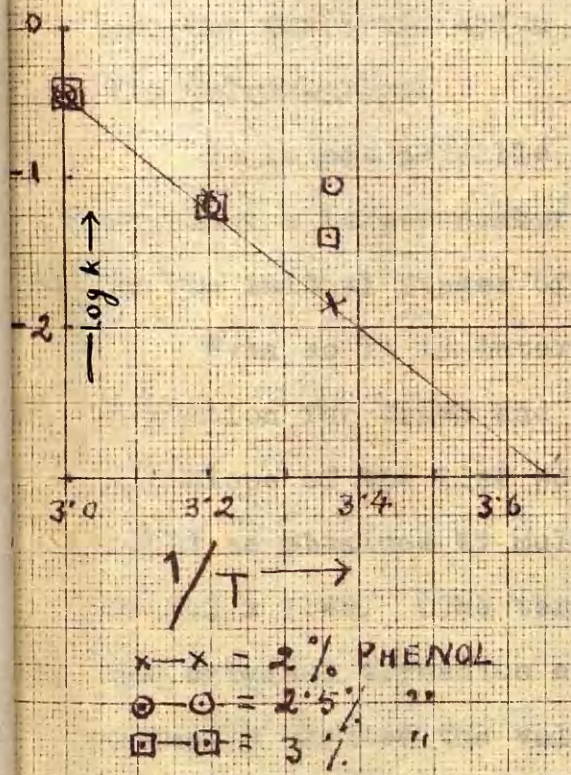


FIG. 26 : DRAWN NYLON

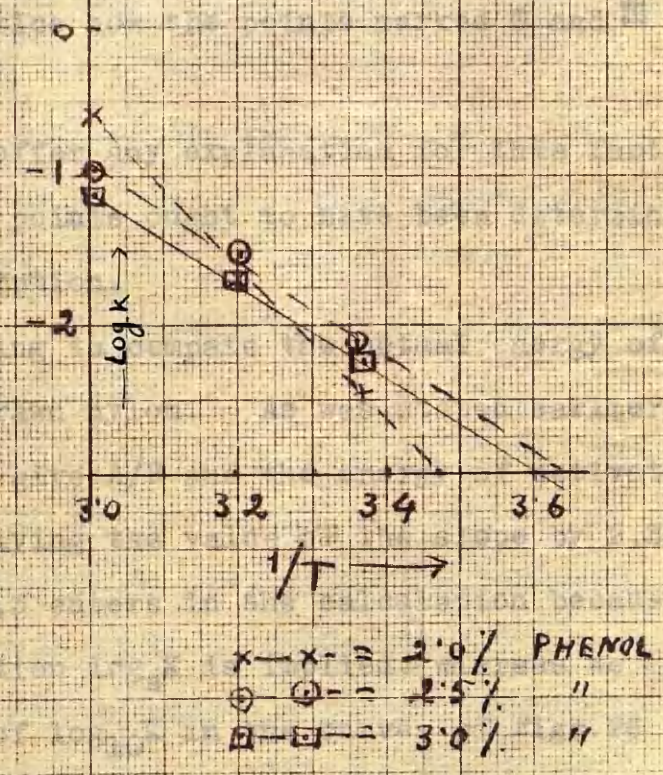


FIG. 27 : UNDRAWN NYLON

ARRHENIUS EQUATION APPLIED TO THE RATE DATA OF AQUEOUS PHENOL ON DRAWN NYLON AND UNDRAWN NYLON. Log. k. PLOTTED Against 1/T.

initial concentration of 2% Phenol, a straight line is obtained for both drawn as well as undrawn nylon. At the two higher concentrations, good straight lines are obtained for undrawn nylon but not for drawn nylon (notice how the points marked ⊙ and ⊡ lie irregularly.)

It is not possible to offer any explanation for this fact. Probably a larger number of points ought to have been determined in the initial stages of sorption.

Even so it is interesting to compare the actual energy of activation for drawn and undrawn nylon. As was stated earlier, the slope of the line would give A/R and the energy of activation would be obtained by multiplying the value of the slope by 2.3 x R or 2.3 x 1.98. (The term 2.3 enters in the calculation because in the original Arrhenius equation $\log_e K$ is implied, whereas we have actually plotted the value of $\log_{10} K$ in the curves of Figs.26 and 27. The energy values calculated are as follows.

Drawn Nylon ..... 17,900 cal. per mol. of phenol sorbed.

Undrawn Nylon ... 24,300 " " " " " "

Here again, it is felt that the difference in the activation energies must be attributed to the difference in the nature of the surfaces of drawn and undrawn nylon. In drawn nylon, the sorption of phenol may be inferred to take place by the rupture of hydrogen

bonds and since the heat of hydrogen bonding and the heat of "bond-:rupture" are of opposite sign, the energy of activation required in this case is smaller. In undrawn nylon, there are free carbonyl radicals where phenol molecules might combine directly and the energy of activation required for such combination is greater. At the higher concentrations of 2.5% and 3% in undrawn nylon (curves 2 and 3 in Fig. 27) the activation energy again falls to about 17,000 calories, probably because, from the start of the absorption, the two types of reactions, bond-breaking and hydrogen bond formation, occur simultaneously.

We are quite conscious that these implications of the results of the heat calculation for the isotherms and rate curves are only speculative. The results however do prove that the mechanism of the sorption of phenol molecules is by no means simple.

Rate of absorption of Aqueous benzoic acid on drawn nylon.

The general procedure and method of analysis was similar to that described on p. 17 . Fig. 28 shows rate curves for sorption of benzoic acid on drawn nylon at five different concentrations at 25°C. Table 23 gives the actual experimental data for these curves. It is to be noted that the rate is dependent on the con-:centrations of the starting bath. The higher the concentration the greater is the amount absorbed in a given time.

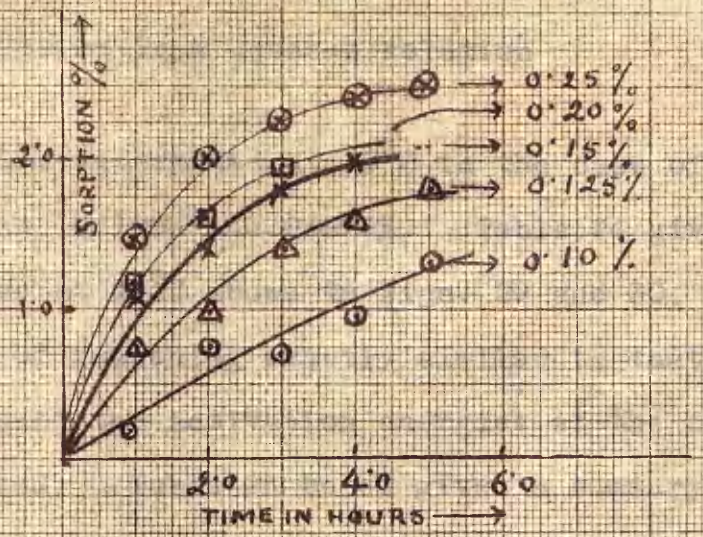


FIG. 28. : RATE OF SORPTION OF BENZOIC ACID ON DRAWN NYLON AT 25° C AT VARIOUS STARTING BATH CONCENTRATIONS.

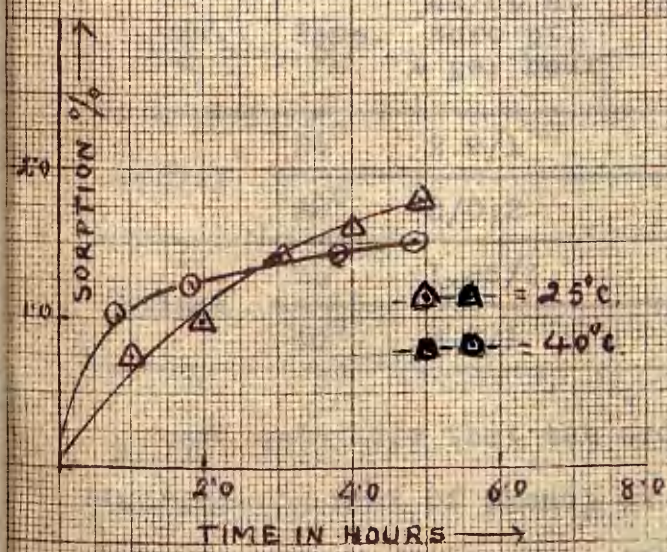


FIG. 29. : EFFECT OF TEMPERATURE ON THE RATE OF SORPTION OF AQUEOUS BENZOIC ACID ON DRAWN NYLON. (STARTING CONC. OF BATH = 0·125 %)

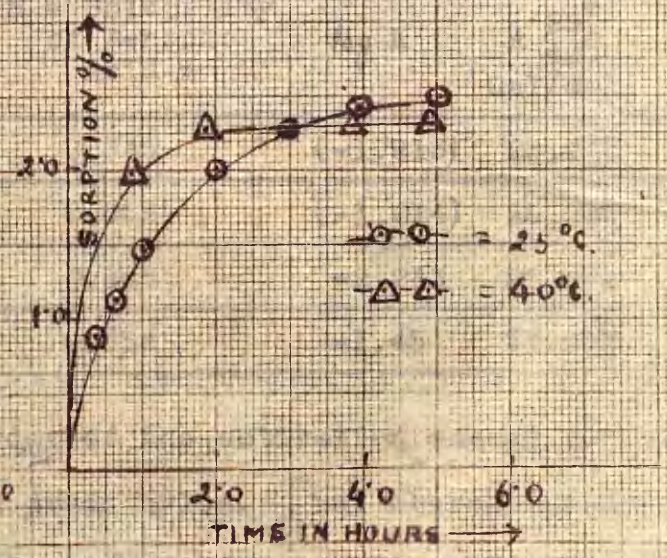


FIG. 30. : EFFECT OF TEMPERATURE ON THE RATE OF SORPTION OF BENZOIC ACID ON DRAWN NYLON. (STARTING CONC OF BATH = 0·275)

Sorption from Aqueous solution

Rates were also determined at 40°C in the case of two initial concentrations, viz. 0·125% and 0·275%. Table 24 gives the data for the rate curves at 40°C shown in Figs. 29 and 30.

By a process of reasoning exactly similar to that described in the case of phenol the activation energies at the zero point have been calculated. Table 25 below gives a summary of the calculations. The correction for solubility was made as in the case of phenol (see p. 52).

TABLE 25.

Heat of activation at the zero point, calculated from the velocity constants by applying the Arrhenius equation.

Conc. %	Temp. °C	dx/dt at zero pt. % per hour	S = Solubility of Benzoic Acid %	log K	$A_{40^\circ}^{25^\circ}$ Cal/mol.
0.275%	25°	2.9/1	0.345	(-1.913)	25,240
	40°	3/0.2	0.555	(-1.014)	25,240
0.125%	25°	1.85/3	0.345	-2.243	22,270
	40°	2.5/1	0.555	-1.45	22,270

We note here that the order of the activation energy is comparable to that of phenol on drawn nylon. But whereas phenol gave an energy of about 17,000 cal/mol, for Benzoic acid the figure is about 22,000 to 25,000 cal/mol. The higher energy might be due

to the higher molecular weight of benzoic acid.

That the activation energy is comparable with that of phenol is significant as supporting the assumption that undissociated molecules of benzoic acid may combine with nylon by hydrogen bonds.

Conclusions

The methods used for the study of sorption from aqueous solu-:tion are those commonly employed, with the difference that we have maintained the material-sorbate ratio (and not the material liquor ratio) a constant. The equilibrium concentration of the bath are expressed as 'relative concentration' to include the effect of the solubility of the sorbate in the solvent. By relative concentra-:tion is meant ~~the ratio of~~ the ratio of the actual concentration of the sorbate in the solvent to its solubility at the temperature under study. Any variations of the solubility of the sorbate with temperature are thus taken into account and the interpretation of the effect of temperature on the course of sorption as well as the heat calculations are more consistent. This was clearly seen in the case of the isotherms of phenol on nylon at different tempera-:tures. Similarly, it was shown how results so expressed indicate that resorcinol has a greater affinity for nylon than phenol where-:as results expressed in the normal way would have led to the erroneous conclusion that the contrary was the case.

Sorption from aqueous solution

The successful application of Langmuir's adsorption mechanism to the isotherms of phenol on nylon is taken to mean that nylon behaves as a uniform surface with sorption sites of identical heats of reaction. It would appear from this that the -NH-CO- groups in the fibre are responsible for the combination of phenol. Heats of reaction between nylon and phenol were calculated with a view to derive support or otherwise to the above assumption. It was found out, however, that the considerations of the exchange of energy during the course of sorption are too complicated. Three contending heats of reaction are to be taken into account, viz. heat of hydrogen bonding, heat of bond-breaking and heat of swelling and contraction. The calculated heat of reaction is a resultant of all these and the heat may be high or low depending on the nature of the nylon fibre.

In spite of low solubility, it was interesting to find that benzoic acid is easily and appreciably sorbed by nylon whereas benzenesulphonic acid was not. Its isotherm was sigmoid as in the case of phenol,and Langmuir's formula could be successfully applied in this case also. All this strongly suggested that the modes of combination of phenol and benzoic acid on nylon was simi-:lar. It is quite likely that this acid and probably many other weak organic acids combine with nylon by hydrogen bonds. Ionic

considerations do not seem to be very important where the com-:pound shows tendency towards hydrogen bonding.

The isotherms of aqueous aniline on drawn and undrawn nylon are rather interesting. At first sight one would conclude from such a result that aniline had an appreciable affinity towards nylon. But as we shall see later, this compound shows no af-:finity for nylon when studied from the vapour phase. We shall have occasion to refer to this point again. It is suggested that aniline does not combine directly with nylon but is adsorbed on a layer of previously adsorbed water molecules.

—x—

II

R E S U L T S A N D D I S C U S S I O N (Continued)

B. Sorption from Vapour phase.

II. RESULTS AND DISCUSSION (Contd.)

B. Sorption from Vapour phase.

(i) **Experimental**

As pointed earlier, the study of sorption from solutions on fibres has some limitations and hence more stress is laid on the vapour phase sorption in this work. The experiments on sorption from solution were made in the hope that it might be possible to correlate the results with those obtained from vapour phase studies.

The experimental technique and apparatus used depended on whether the vapour to be studied had an appreciable pressure at room temperature or not. Thus when sorptions of vapours of water, methyl alcohol, ethyl alcohol, acetone, pyridine, acetic acid, etc. were to be studied, it was possible to work at about 25°C. When vapours of phenol, β-naphthol or benzoic acid, etc. were to be studied, a very much higher temperature (50° to 80°C for phenol and 120°C for β-naphthol and benzoic acid) had to be used. The apparatus used for lower temperatures was different from that used for higher temperatures.

There are two common features in both types of experiments. (i) The use of high vacuum for cleaning the surface of the fibre and (ii) The use of a glass spiral for weighing the sorbent before and after sorption.

The need for high vacuum as well as the method of using the glass spiral, etc. is explained in detail in Appendix 2. We have

purposely not included the details here to keep a continuity in the discussion of our results. Suffice it to mention here only some important points regarding the experimental procedure. We note that:-

(i) As sorbents, wool, drawn nylon and undrawn nylon have been studied.

(ii) As sorbates, the following compounds have been used: water, methyl alcohol, ethyl alcohol, ethyl acetate, methyl malonic ester, acetone, pyridine, benzene, acetic acid, dry hydrochloric acid gas, phenol, β-naphthol, benzoic acid, alizarine and aniline.

(iii) Rate curves as well as isotherms were determined. For water, methyl alcohol and ethyl alcohol, isotherms were determined. For all the higher melting compounds no isotherms could be determined because the temperatures were too high for suitable thermostatic control. Moreover most of the hydroxy compounds did not reach equilibrium with the fibre.

(iv) In some cases it was desired to see the effect of surface area on sorption. Nylon powder was prepared for this purpose as follows:-

1 g. of nylon was dissolved in 30 g. molten phenol and the

whole precipitated by adding to two litres of hot boiling water with constant stirring. The precipitated nylon was then filtered and washed with distilled water. It was found that washing of the last traces of phenol was very slow and incomplete. Hence the sample was subjected to Soxhlet extraction with 95% alcohol until free from phenol.

(v) Where higher temperatures had to be used, a six litre Pyrex-glass beaker containing liquid paraffin was used as a ther-:mostat. The liquid bulb and the tube carrying the glass spiral were both immersed in this bath. The degassing of the fibre was done by vacuum. (The details and the apparatus are described in Appendix 2). The heating was done electrically and the liquid was stirred by means of a circulating pump. Flexible copper tubing was used for conveying the circulating liquor because paraf-:fin readily destroys rubber.

(vi) The glass spiral showed a tendency to change in length after heating. But if the spring was heated for eight hours at 200°C, the defect was corrected. Repeated reheatings of the spiral at 100°-140°C. did not alter its length or sensitivity after such a treatment.

(vii) The diameter of the spring fibre as well as the number of turns per inch were so chosen that the spiral showed an

extension of about 12-15 cm. per gm. of load. The maximum load that the spiral could carry was about 0·5 g. but actually 0·15 to 0·3 g. of the fibre sample was used for experiments. The sensi-:tivity was enough to give an accuracy of ±1% in weights.

(viii) The spiral length was read by a cathetometer rigidly mounted on a wooden stand. The floor of the room in which these experiments were carried out was made of wood and it tended to vibrate and alter the readings, so that readings for both the top end and the lower end of the spring were taken. Particular care was taken to see that floor vibrations did not cause any variation for each set of readings.

(ix) The cathetometer could be read correctly to 0·001 cm. It was always ensured that the lower end and the upper end of the spring were on one vertical line so that when readings were taken, both ends could be focussed at or very near the centre of the cross wires in the eye-piece of the cathetometer. It is import-:ant to see that there is no parallax between the point of the spring and the centre of the eye-piece.

(x) When isotherms were to be determined at or near 25°C, the whole apparatus was enclosed in an air thermostat. (For de-:tails see Appendix 2). An additional water thermostat was pro-:vided round the tube carrying the spiral and the fibre. The liquid whose vapour was to be studied was thus kept at the temper-

:ature of the air thermostat, whereas the temperature of the sor-:bent could be varied at will by adjusting the temperature of the water thermostat. The temperature of the water thermostat was never more than 10 to 15°C. higher than that of the air thermostat.

(xi) All stop-cocks used were of Edwards' special high-vacuum type. Edwards "High-Vacuum" silicone grease was used on all the cocks.

(xii) High vacuum was produced by a combination of an Edwards two-stage mercury diffusion pump and a backing pump capable of pro-:ducing 0·01 mm. vacuum. The resultant vacuum attained was 0·0005 to 0·00001 mm. It was measured by a McLeod gauge. Phos-:phorus pentoxide, contained in a dish, was placed between the diffusion pump and the backing pump to facilitate drying of the apparatus and the fibre.

(ii) Some Preliminary Observations

A number of minor points, such as the effect of temperature on the spiral behaviour, the reliability and repeatability of the equilibrium sorption value, were experimentally checked. It is to be noted that McBain's (64) original suggestion was to use a sensitive-quartz spiral for the measurement of sorption. It was necessary to use quartz because the temperatures used by him were

in the range of 400°C. to 500°C. We have used a glass spiral. Admittedly silica or quartz is a better material both from the point of view of resistance to chemical action and constancy in sensitivity. But our decision to use glass was in the first in-:stance due to non-availability of a silica spiral. Secondly, it was considered that glass should be suitable under the parti-:cular circumstances of our experiments. In Table 8, are listed values for the coefficients of thermal expansion for a few metals and for glass and silica. It will be noted that whereas quartz has as low a value as $5 \cdot 8 \times 10^{-7}$, most varieties of glass and dif-:ferent metals have a very large thermal expansion coefficient.

Fig. 30a gives the effect of temperature on expansion for various materials (65). It is to be noted that fused silica has almost negligible expansion within as wide a range as 0° to 600°C. It has also a perfect linear relationship. Pyrex glass is the next best. As long as the temperature does not exceed 300°C, it also shows a linearity.

For these reasons, one would expect that a glass spiral should give satisfactory results if used, say, below 200°C. While dealing with textile fibres, we cannot go beyond 100 to 110° C. without damaging them. It was therefore decided to try a Pyrex glass spring. In Tables 26 and 27 are given typical load-extension values for two glass springs, one having a fibre diameter

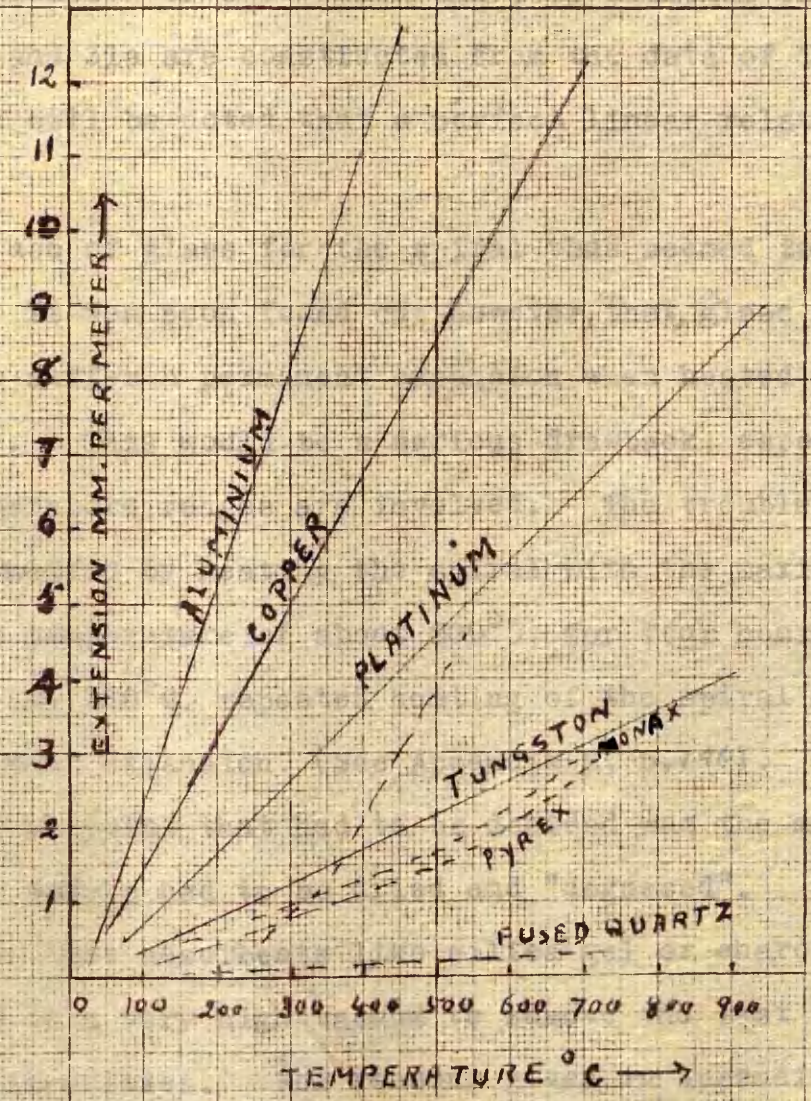
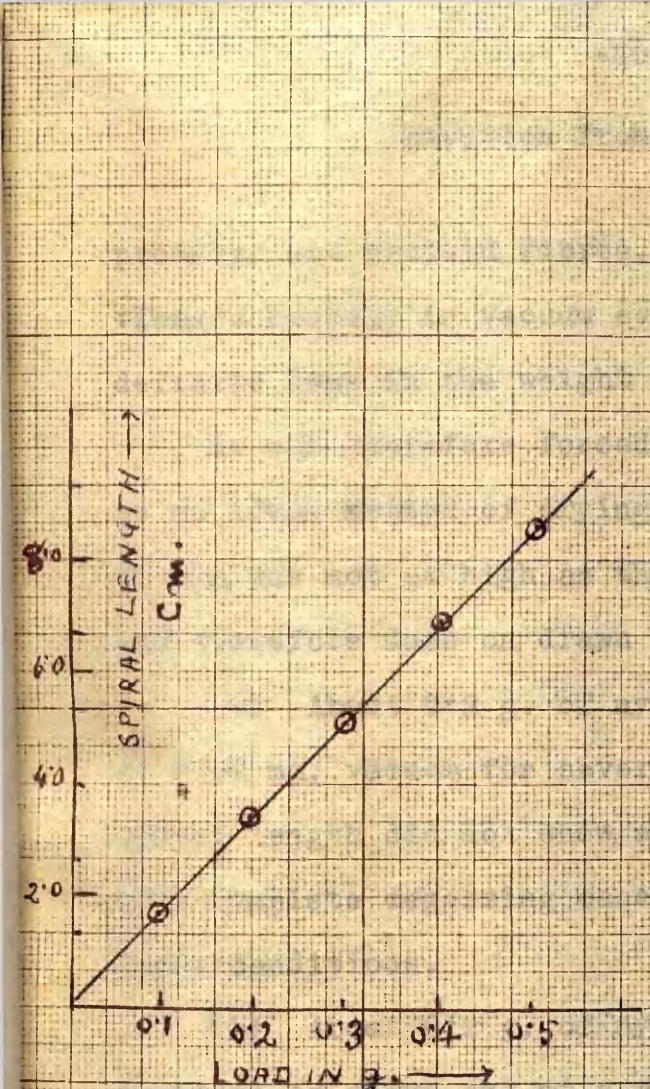


FIG. 30 a. : VARIATION OF EXTENSION WITH TEMPERATURE FOR QUARTZ, GLASS AND OTHER METALS.

of 0·008 inch and coil diameter of 0·75 inch and the other having a fibre diameter of 0·009 inch and coil diameter of 0·5 inch. Figs. 31 and 31a are constructed from the data of Tables 26 and 27 and it will be noted that a perfect linear relationship is ob-:tained.

The use of glass for the spiral thus seemed to be quite pos-:sible. It was soon found out however, that, glass showed a ten-:dency to suffer a permanent expansion when heated under load for some time. This would be a serious drawback, especially when wide temperature ranges are involved. The trouble, however, was easily remedied by heating the spiral with the maximum permissible load at a temperature of about 200°C. for four hours. At tempera-:tures below 150°C. repeated heating of the spiral did not show any permanent expansion. (See Appendix 2, p.196).

Another point that had to be decided was the manner in which the fibre sample had to be dried and "degassed". It is common experience that adsorbents like silica gel or charcoal must be subjected to a very high vacuum to remove the last traces of the adsorbed impurities. For reasons given in Appendix 2, we had al-:ready decided to use a vacuum as high as 0·0005 mm. But what should be the temperature of degassing? Bull (44) discusses this point in detail while studying the method of drying a number of



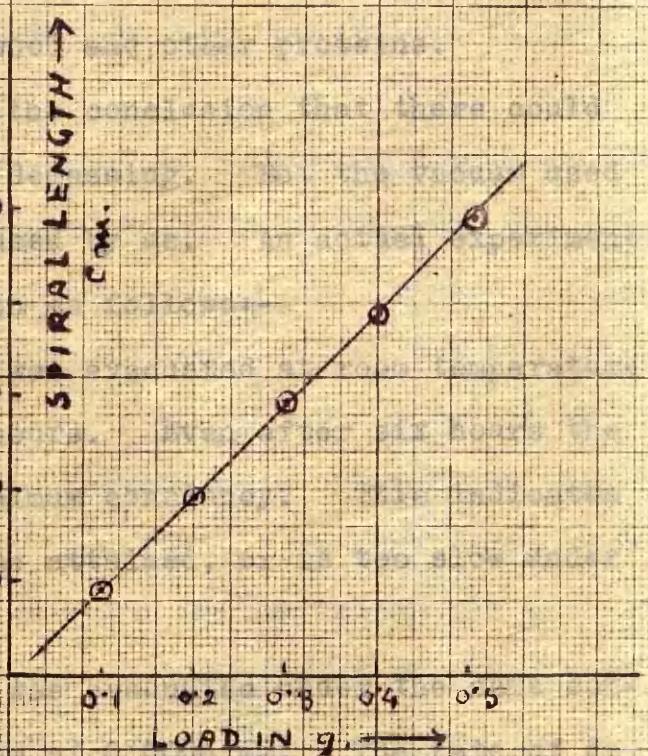
(SPIRAL NO. 1)

FIG. 31

COIL DIA. = 3/4"

FIBRE DIA. = 0·008"

TURNS PER INCH = 12.



SPIRAL NO. 2

FIG. 31a.

COIL DIA. = 1/2"

FIBRE DIA. = 0·009"

TURNS PER INCH = 12

proteins and protein fibres. He shows conclusively that pro-:longed heating in vacuum even at 100°C. produced a slight but definite loss in the weight of wool and other proteins.

He was therefore forced to the conclusion that there could be no ideal method of drying or degassing. But the vacuum used by him was not as high as that used by us. An actual experiment was therefore done on drawn nylon as follows:-

(a) About 0·2 g. of nylon was evacuated at room temperature at 0·02 mm. vacuum for several hours. Even after six hours the spiral length did not show a minimum constancy. This indicates that complete degassing cannot be attained, or is too slow under these conditions.

(b) About 0·2 g. of nylon was evacuated under the same con-:ditions as above but at a vacuum of 0·0005 mm. The rate of de-:gassing improved considerably and in about $3\frac{1}{2}$ hours the spiral showed a constant length. It appeared therefore that the degass-:ing was complete. It was quite likely however that the constancy might only be apparent and not real; the rate of degassing might be imperceptibly low. To check this point, the following proced-:ure was carried out:-

(c) The same sample of nylon was heated at 100°C. while still maintaining the high vacuum. It was found that within about 10

minutes' heating the sample registered a further loss in weight of about 1 to 1·25%.

It was therefore apparent that a higher temperature is perhaps as important as high vacuum.

In spite of the above observation, we decided not to heat the fibre to a high temperature, because the risk of changing the surface structure due to high temperature was always there. Hence it was arbitrarily decided to carry out degassing at the temperature of the experiment.

The results presented in this section were obtained in the initial stages of building up the apparatus. In some cases (due to non-availability of a diffusion pump) the degassing was done at only 0·01 mm. vacuum. After a time a glass diffusion pump was available. It could not, however, give a vacuum higher than 0·001 mm. Further, no air thermostat was constructed round the sorption apparatus as a whole. Thus, though the temperature of the adsorbent fibre was accurately controlled by immersing the sorption tube in a water thermostat, the temperature of the liquid in the sorbate reservoir fluctuated with the room temperature. The results presented therefore are to be taken with reserve. The experiments were useful as practice in the high vacuum technique and the handling of the delicate spiral. They are therefore presented below.

Sorption from vapour phase

A number of liquids were studied to obtain a rough idea as to the approximate quantities sorbed on nylon. The following Table summarises the results.

TABLE 28

Equilibrium - Sorption of Different Vapours on Drawn Nylon.

Vapour	Vapour Pressure mm.	Temp. °C.	Sorption (%)
Water	15	25	3.7
Methyl alcohol	98	25	4.6
Ethyl alcohol	36	25	3.8
Ethyl acetate	55	25	0.3
Acetone	70	20	1.5
Pyridine	10	14-18 ... (No thermostat)	Negligible
Phenol	Negligible	, 25	15.0 (No equilibrium)
Resorcinol	"	25	Nil

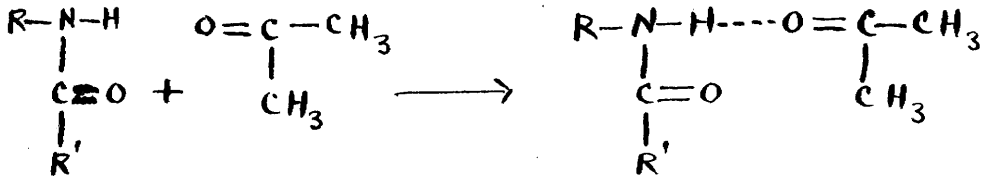
The behaviour of phenol vapour is very interesting. It shows that even at negligible vapour pressure the quantity sorbed is very great.

It will be noted that every liquid that shows any appreciable sorption in the above list has a functional hydroxy group.

The low sorption in the case of ethyl acetate is remarkable; because ethyl alcohol has an appreciable sorption, the belief that

the hydroxy group has an important role in sorption is thus strengthened.

Another interesting point to note is the very low sorption of acetone. If the sorption were assumed to be due to hydrogen bond-:ing and if there were any appreciable number of free -NH-CO- groups (not involved in internal hydrogen bonding) in drawn nylon, one would expect that the carbonyl oxygen of acetone should bind itself with the amido hydrogen thus:-



The fact that only about 1·5% of acetone is taken up by nylon indicates that there are probably very few or no 'free' -NH-CO- groups in nylon. This could be regarded as an indirect evidence for the 'coiled-chain' structure given to synthetic polyamides by Bamford and Hanby (see p.46).

It is to be recalled that while discussing the action of aqueous phenol on nylon, a suggestion was made that the molecules of phenol have a higher affinity for nylon than has water and hence replace the latter from the surface of the fibre. That the assump-:tion was justified is shown by the very high percentage of sorp-:tion observed here.

Sorption from vapour phase

Resorcinol has a much higher boiling point than phenol and the absence of any sorption of resorcinol at 25°C. might be due to its very low vapour pressure. Actually resorcinol has a greater affinity for nylon than phenol, as we have observed on p. 34 .

II .

[illegible]

II C.

RATE STUDIES FROM THE VAPOUR PHASE

II

C : Rate Studies from the Vapour Phase

(i) General.

The study of vapour phase sorption, like all physicochemical studies can be divided into two parts representing kinetics and thermodyanamics. The former deals with rate processes and the latter with equilibria.

A study of the available literature on sorption shows that a comparatively small amount of work has been done on rate processes. Perhaps the main reason is that true adsorption phenomena are too rapid to measure. But this is not always true. There are many processes where the rate is not only measurable but quite appreciably slow. The slowness of the measured rate might be due to various reasons. In the first instance it may be due to the time required to dissipate the heat of sorption. As an instance, we may refer to King's work (52). He studied the rate of up-take of water vapour by wool. He also determined experimentally the rise in temperature of the wool fibre during sorption and demonstrated that a very considerable rise in temperature caused the process of sorption to proceed slowly. Secondly, the slowness of the observed rate may be due to the inaccessibility of the inner surface of the sorbent: the sorbate molecules might diffuse into the pores of the adsorbent and this might be a slow process depending on the pore size of the adsorbent and the molecular size of the adsorbate.

Rate Studies from vapour phase

Lastly, the rapidity or the slowness of an adsorption reaction may be entirely due to the process involving small or large activation energies respectively. This point has been discussed by Taylor (66). He points out that a simple adsorption mechanism derived from Langmuir's kinetic consideration is no longer adequate to ex-:plain abnormalities in the data of sorption. To quote his own words:-

"The assumption that all processes of adsorption have their characteristic activation energies permits a single general treat-:ment of adsorption, inclusive of processes which hitherto have been considered separate and unrelated.....The only essential distinction between "secondary" and "primary" adsorption or between "reversible" and "irreversible" adsorption is that the secondary or reversible adsorption processes are adsorptions nor-:mally with small heats of adsorption and small activation energy and that in the so-called primary adsorptions moderate or large energies of activation are involved, frequently with high heats of adsorption. The velocity of these latter processes may indeed be very slow....."

It will be clear from the above that the following points must be kept in mind while studying sorption rates on textile fibres:-

Rate Studies from vapour phase

(i) The surface of the fibre and its pore structure: The rate will clearly depend on the relative size of the pores and the adsorbate molecules.

(ii) The heat of adsorption and the energy of activation characteristic of the particular process: The higher the energy of activation, the slower the process.

(iii) It is therefore unlikely that a single general theory of sorption rate could be put forward to explain all the avail-:able rate data. Each sorption process must be viewed separate-:ly, though the application of general theories might throw some light on the mechanism of sorption.

We shall now consider two fundamental theories of sorption rates. One is due to McBain and the other to Langmuir. There are various other theories which could be regarded as more or less modified forms of these two. We shall therefore consider these two in detail. Later, we shall apply these theories to our own experimental results to see if they assist us in under-:standing the behaviour of wool and nylon towards various vapours.

McBain's theory was based on the consideration of the behav-:iour of hydrogen towards charcoal (67). He observed that the absorption consisted of two distinct phenomena. He called one of these adsorption and believed that its rate was instantaneous;

he also believed that the other process was solid solution and derived an expression for its rate from Fick's diffusion law. The equation is,

$$Q = \frac{4CL}{2}\left\{\frac{\pi^2}{8} - \left(e^{-at} + \frac{1}{9}\cdot e^{-9at} + \frac{1}{25}e^{-25\,at} + \ldots\right)\right\} \quad \ldots(1$$

where

Q = amount of gas that has diffused through unit surface at time t,

C = concentration in the gas phase (assumed to remain constant),

L = total thickness of the solid,

$a = D\pi^2/L^2$, and

D = diffusion constant.

If a considerable fraction of the final amount is already dissolved in the solid, all terms but the first in the parenthesis can be neglected to a very good approximation. One obtains then

$$Q = \frac{4CL}{\pi^2}\left(\frac{\pi^2}{8} - e^{-k't}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

The above can be rewritten as

$$Q = A - B\cdot e^{-k't} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where $A = \frac{CL}{2}$ and $B = \frac{4CL}{\pi^2}$

or $$\frac{A - Q}{B} = e^{-kt} \quad \ldots\ldots(4)$$

or $$\text{Ln}\frac{A - Q}{B} = -kt \quad \ldots\ldots(5)$$

Since A and B are constants which can be readily evaluated from the Q vs t graph i.e. from the rate curves, equation 5 is now in a form which can be tested.§ A plot of t against $\text{Ln}\frac{A - Q}{B}$ should give a straight line if the equation is obeyed. When it is obeyed, the inference that the sorption process is one of diffusion or solid solution would be justified. Otherwise one must look elsewhere for the causes of discrepancies. We have used the above equation from time to time for our data. The significance will be discussed under appropriate headings.

As mentioned earlier, we shall now consider Langmuir's theory (31). The fundamental concepts of Langmuir are detailed in Appendix 1, where his isotherm equation is derived. Suffice it to note here that the experimentally-measured rate is the difference between the rate at which molecules condense on the

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§ The constants A and B are evaluated by choosing points t_1, t_2, t_3 on the time axis such that $t_1 + t_3 = 2t_2$, and solving $A - Q_1$, $A - Q_2$, $A - Q_3$ etc. by equating with $B.e^{-kt_1}$, $B.e^{-kt_2}$ etc. in the usual manner.

surface and the rate at which they evaporate. If the rate is determined at constant pressure, it is given by

$$\frac{d\theta}{dt} = k_1 (1-\theta) - k_2\theta \quad \ldots\ldots\ldots\

Rate Studies from vapour phase

Now let C_F be the amount of gas sorbed per unit weight of the fibre at time t and C_e be the amount sorbed at equilibrium. Obviously

$$\frac{C_F}{C_e} = \frac{\theta}{\theta_e} \quad \text{.....(11)}$$

Substituting in 10, we have

$$\frac{C_F}{C_e} = 1 - e^{-kt} \quad \text{.....(12)}$$

$$\text{or} \quad \log_e \frac{C_e}{C_e - C_F} = Kt \quad \text{.....(13)}$$

Whenever equilibrium quantities of sorption can be experimentally determined, equation 13 can be used to test the experimental results. If the surface behaves as a "free" and uniform surface with identical sorptive centres at all points of the surface, one would expect the above equation to be obeyed. A plot of $\log_e \frac{C_e}{C_e - C_F}$ against t should give a straight line. Wherever possible this equation has been used in the present work.

There is yet another aspect of the rate studies. As will be evident from the results presented below, most of the high-melting compounds studied did not attain any equilibrium. It would serve little purpose to try and interpret the data in terms of the Langmuir equation derived above. In such cases, the

velocity constants could be calculated from the rate curves. If the rate data at different temperatures were known, the activation energies of the sorption could be calculated by applying the Arrhenius equation. A similar procedure was followed for calculating the activation energies of phenol and benzoic acid for nylon from aqueous solutions (p. 52). This activation energy could be calculated at the zero point for the bare surface as in the case of aqueous phenol. It could also be calculated for the average course of reaction if the rate curves showed constant velocity-coefficients.

Rate Studies from vapour phase (Contd)

(ii) Water, Methyl Alcohol and Ethyl Alcohol on Drawn Nylon:

We shall now proceed with the discussion of results. As pointed out earlier, rate determinations have been made for various compounds on nylon and wool. The sorbates studied include hydroxy compounds with low molecular size such as water and methyl alcohol on the one hand and high molecular size compounds such as phenol, benzoic acid and alizarine on the other. Also, to study the effect of acidity, comparison of rates of hydrochloric acid and acetic acid are made. The results are presented under different heads. The broad aspects of the experimental technique are already discussed on p. 59 , and the details of the experimental procedure are included in Appendix 2. We shall therefore not repeat any experimental details here.

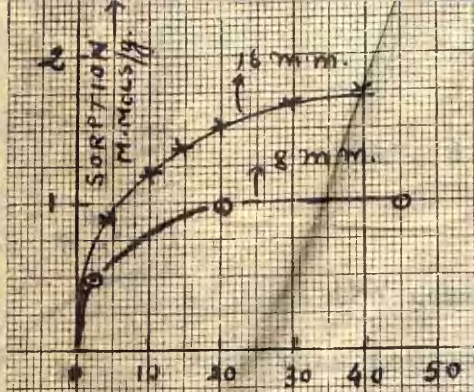
In all the cases the temperature of sorption was 26°C. In the case of water, the rate has been measured at 8 mm. and 16 mm. For methyl alcohol the rate has been measured at three different pressures, 13.5 mm. 36 mm. and 94 mm. For ethyl alcohol the rate has been measured at one pressure only, 40 mm. The curve for ethyl alcohol was not pursued up to equilibrium because the rate was too slow to measure. The data are given in Tables 29-31.

Rate Studies from vapour phase

Fig. 32 shows rate curves for water; Fig. 33 those for methyl alcohol and Fig. 34 the one for ethyl alcohol.

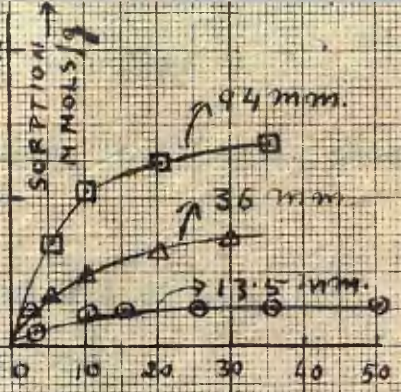
It is to be noted that at saturation pressures the rates of sorption show a graded behaviour. The rate of sorption of water is greater than that of methyl alcohol which in turn is very much greater than that for ethyl alcohol. Further, the equilibrium quantity of water sorbed is greater than that of either of the alcohols. (See Figs. 32, 33 and 34). Thus the time of equili-:brium for water is only 40 min., that for methyl alcohol is 90 min; (The curve for ethyl alcohol, Fig. 34, is not shown for the whole course of the rate. But it was noticed that equilibrium was not attained even after 20 hrs.)

A possible reason for this is that the rate depends on the size of the adsorbate molecules. This is equivalent to assuming that diffusion is the rate controlling process. To see if this was so, the data of Figs. 32, 33 and 34 were tested by applying McBain's diffusion equation (p.74, equation 5). In Figs. 35, 36 and 37, these curves are shown. It will be noted that except at very low pressures, the expected straight line relationship is observed. It is to be noted however that the low pressure data (water vapour at 8 m.m. and methyl alcohol at 13.5 m.m.) do not obey McBain's equation. (These curves are not shown in the figure) Neglecting the low pressure curves, where the effect of pure sur-:face adsorption would be predominant, it is to be seen that thes



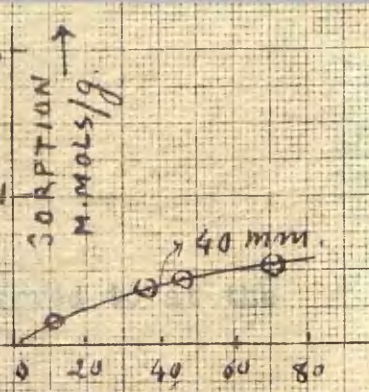
(WATER VAPOUR)

FIG. 32.



(METHYL ALCOHOL)

FIG. 33.



(ETHYL ALCOHOL)

FIG. 34.

← RATE CURVES FOR VAPOURS OF WATER, METHYL ALCOHOL AND ETHYL ALCOHOL ON DRAWN NYLON →

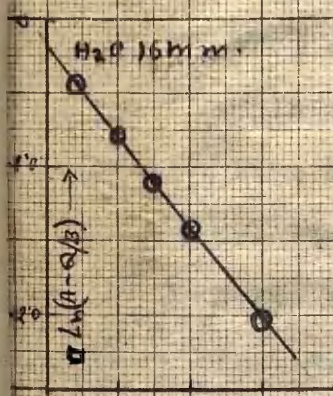


FIG. 35

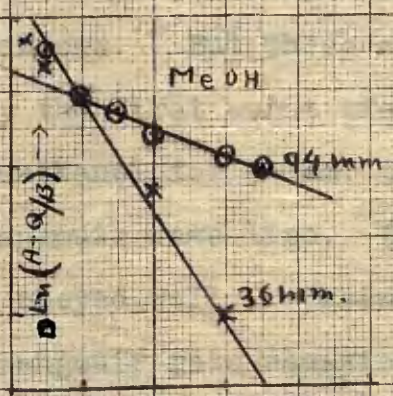


FIG. 36

FIG. 37

McBAIN'S DIFFUSION EQUATION APPLIED TO THE DATA OF FIGS 32, 33 & 34.

results support the conclusions of King (53) referred to at the beginning of this section.

Langmuir's rate equation (p.76) on the other hand considers the adsorbent surface as uniform and assumes the rate to be mainly governed by surface considerations. Figs. 38, 39 and 40 show curves drawn by applying equation 13 (p.76) as stated. It is very interesting to note that in general the equation is obeyed.

It is true that the curves for methanol and ethanol at saturation show slight deviations. But these are not very significant. In ethanol only the first point lies away from the straight line whereas in methanol for 94 mm. there is a slight and gradual bend in the Langmuir rate line. (See Figs. 38 and 40) For water the equation is obeyed well. Taking the limitations of the derivation of the Langmuir rate equation into consideration, we can safely say that for all the three vapours studied, the rate data indicate that nylon behaves as a free and uniform surface with identical sorption centres for all the three vapours. In the physical sense, this can be taken to mean that the vapours of water or the two alcohols are truly adsorbed by the surface of nylon and that the amorphous and crystalline nature of nylon has

FIG. 38

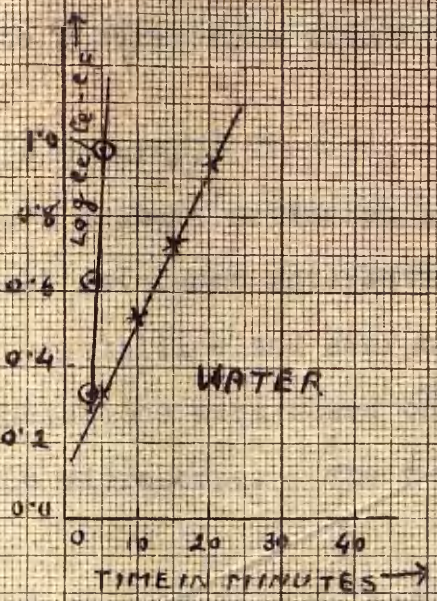


FIG. 39.

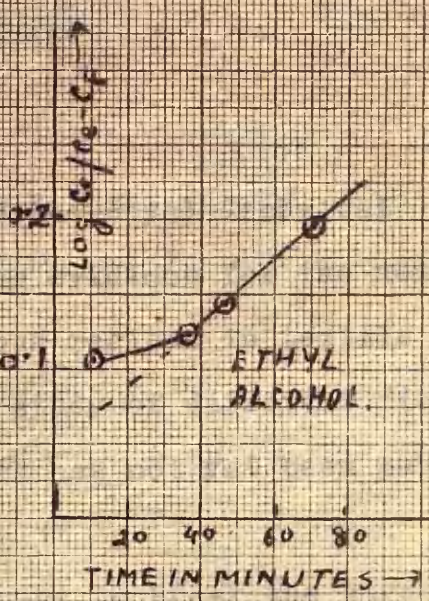


FIG. 40

← LANGMUIR RATE EQUATION APPLIED TO RATE DATA OF VAPOURS OF WATER, METHYL ALCOHOL AND ETHYL ALCOHOL ON DRAWN NYLON. →

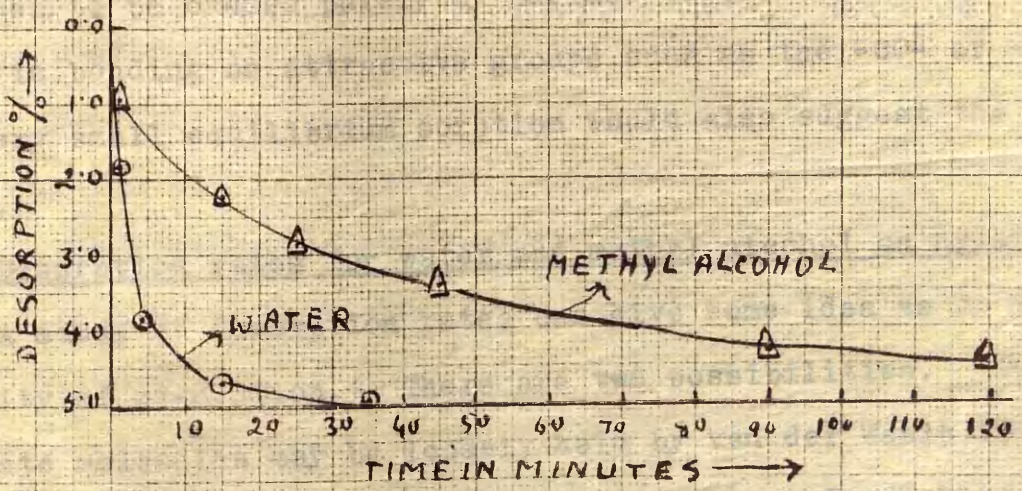


FIG. 41.

RATE OF DESORPTION OF VAPOURS OF WATER AND METHYL ALCOHOL FROM DRAWN NYLON.

not any great part to play.

(Astbury, in a lecture delivered at the Royal Technical College (Oct. 1949) gave some interesting evidence for the non-existence of any crystalline and amorphous regions in textile fibres. His conclusions were based on study of different fibres under the electron microscope. The work has not yet been pub-:lished).

Water and the two alcohols do not seem to break the struc-:ture of the fibre as phenol does. That is why Langmuir's equa-:tion can be successfully applied to the rate data. Further, for the same reason, we have to assume the sorption in these in-:stances to be caused purely by surface forces and not by any specific bonding on attractive groups such as the -CO- or -NH-CO-. The very small equilibrium sorption would also suggest the same thing.

Desorption rates for water and methyl alcohol on nylon.

A study of desorption rates can give some idea as to the tenacity of adsorption. There are two possibilities. The ad-:sorbate molecules may be loosely held by van der Waals forces and may involve negligible activation energy. In such a case, the time required to reach equilibrium and the time for complete desorption should be identical. On the other hand, the process

of adsorption might involve appreciable activation energy. In such a case the molecules will be held more strongly and under isothermal conditions the time of desorption may be appreciably greater.

In Fig. 41 are shown two curves showing the rates of desorp-:tion for water and methyl alcohol. It is to be noted that in the case of water, complete desorption is attained in 40 min. It will be recalled (p. 79) that the time of equilibrium for water was about 40 min. It would therefore appear that the forces of attraction between the surface of nylon and water molecules are of a weak or secondary nature. In the case of methyl alcohol, how-:ever, it will be observed from Fig. 41 that even after 120 min. about 0.5% of the alcohol is still left on the fibre. It was, however, possible to remove the alcohol completely by continuing the desorption for 3 hrs. more. The time required for equili-:brium to be attained in sorption was about 90 min. The affinity of the methyl alcohol towards nylon must therefore be greater than that of water.

It is quite likely that the affinity increases with molecular size. It was qualitatively found that desorption was still more difficult for ethyl alcohol.

II C. Rate Studies from vapour phase (continued)

(iii) Rate of sorption of phenol vapour on nylon and wool.

It is well known that phenol dissolves nylon. The exact mechanism of the solution of nylon in phenol is not yet known. The vapour phase study of phenol was undertaken to see if any light could be thrown on the nature of binding between phenol and nylon. Sorption studies from solution enabled us to come to some conclusions. It was observed that undrawn nylon and drawn nylon show a marked difference in their behaviour with phenol. In one case (undrawn nylon) the sorption appears to take place on account of combination with free -NH-CO- groups followed by rup-:ture of internal hydrogen bonds. In the other (drawn nylon) rupture of internal bonds was followed by severe contraction of the molecular chains. In either case, the influence of water on the sorption of phenol is negligible. This in fact enabled us to apply Langmuir's kinetic considerations to derive an isotherm equation for the sorption of aqueous phenol on nylon. Study of vapour phase sorption might throw a better light on the subject.

A comparison of the behaviour of wool and nylon would also be interesting. Vallance (68) (unpublished work) has studied the sorption of aqueous phenol on wool and has found a character-:istic break point at about 0·80 millimole sorption per g. of fibre. His isotherm for aqueous phenol on wool is reproduced in

Rate Studies from vapour phase

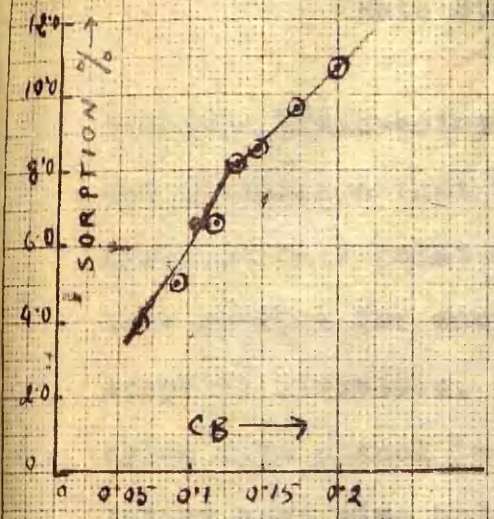
Fig. 42. The absence of a sigmoid shape for the isotherm is remarkable. This would suggest some difference in the peptide structures of wool and nylon. Rates of sorption have been studied for the two varieties of nylon and wool in order to see if the data would demonstrate the difference in their structures.

The two types of nylon fibre were scoured in the same way as in previous experiments. Root ends of fleece wool were pre-treated as follows:-

The fibre was washed in a dilute solution of Lissapol N (0·1%) and rinsed well in distilled water. It was then rinsed with 95% alcohol, squeezed and dried at 60°C. The dry fibre was extracted with ether in a Soxhlet apparatus for 24 hrs., dried, rinsed with distilled water and finally dried again at 60°C. It was then conditioned at room temperature (about 15°C) for 48 hrs. and bottled.

Rate of sorption at 25°C. Drawn nylon and wool

Tables 32 and 33 give rate data for the two fibres. Phenol has a negligibly low pressure at room temperature, and yet in both cases there is appreciable sorption. It is also observed from Fig. 43 that nylon shows a very much higher rate of sorption than that for wool. In both cases equilibrium was not attained. Furthermore, there is a definite break-point at 1 m.mol/g sorp-:tion in drawn nylon. This is significant and corresponds to



EQUILIBRIUM CONC. OF BATH g/100 c.c.

FIG. 42.

SORPTION ISOTHERM FOR AQUEOUS PHENOL ON WOOL. AT 25°C.

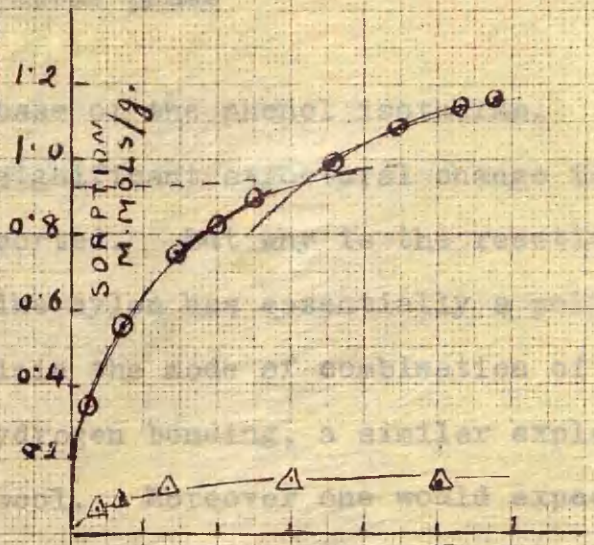


FIG. 43.

RATE OF PHENOL VAPOUR ON DRAWN NYLON & WOOL AT 25°C.

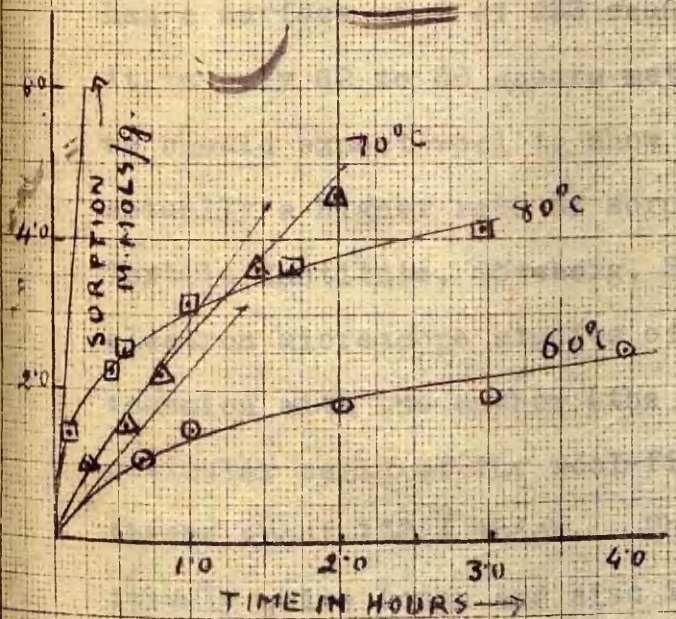


FIG. 44

RATE OF SORPTION OF PHENOL VAPOUR ON WOOL

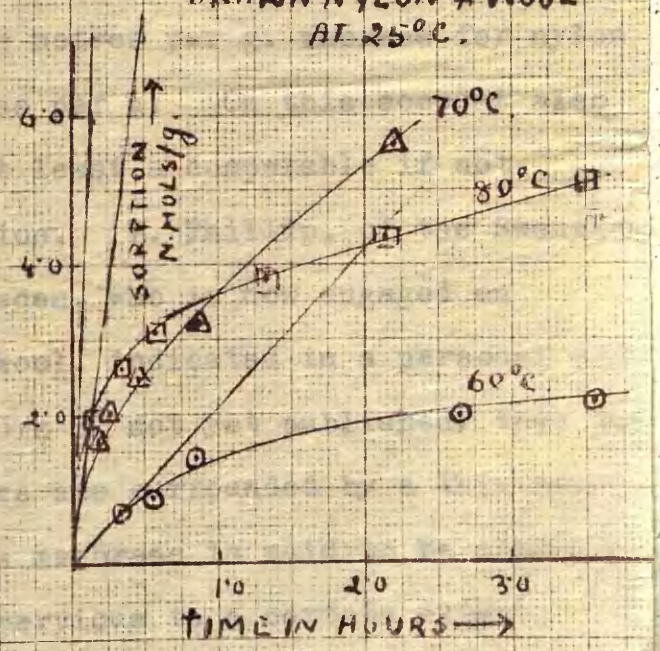


FIG. 45

RATE OF SORPTION OF PHENOL VAPOUR ON UNDRAWN NYLON.

the same break-point as in the case of the phenol isotherms. Our conclusion that there is a significant structural change in nylon at this point is thus supported. But why is the reaction rate so slow for wool? Wool like nylon has essentially a poly-:peptide structure. If we explain the mode of combination of nylon with phenol in terms of hydrogen bonding, a similar explan-:ation must also hold true for wool. Moreover one would expect wool to have a much larger surface area than nylon. Bull (44) has calculated the effective surface areas of wool and nylon on the basis of analysis of water-isotherms and concludes that wool has a surface area of 233 square metres per g. whereas for nylon it is only 62 to 68 square metres per g. On this account also we should expect wool to show at least a comparable if not actually a higher rate of sorption. B. Phillip, of the Swenska-Textile Institute, Göteborg, Sweden, who is now engaged on electron microscope studies of wool, indicated in a personal dis-:cussion with the author (the work is not yet published) that the cuticular cells of the wool-fibre are surrounded by a thin mem-:brane about 100 Å thick. This membrane is said to be compara-:tively quite tough and also impervious to a certain extent. Not very much is yet known about the nature of this membrane. But there seems to be no doubt that such a membrane actually

exists. It may very well be that the slowness of the phenol sorption on wool is due to the phenol molecules not being able to penetrate the membrane and reach the inner surface of the fibre.

Rate of sorption of phenol on nylon and wool at higher temperatures, viz. 60°, 70° and 80°C.

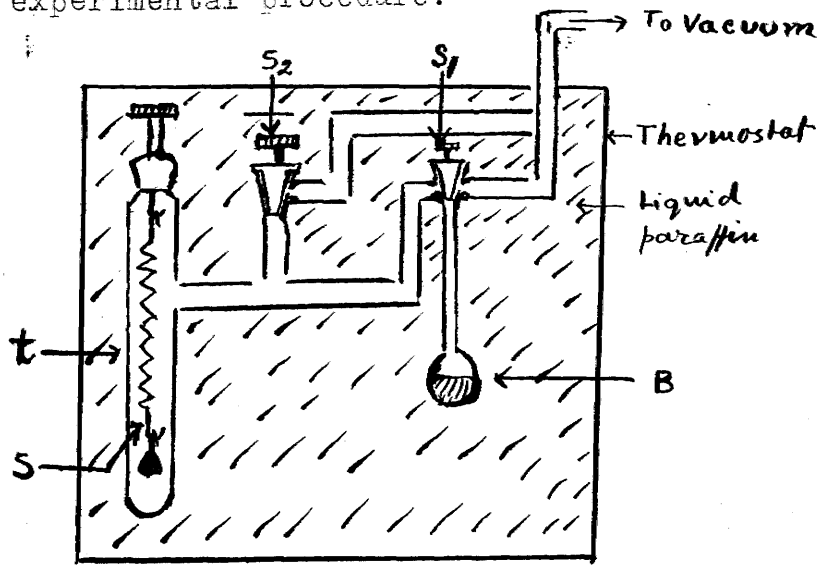
Sorption studies at temperatures appreciably higher than the room temperature have so far not been reported in the literature. An important advantage with the technique of vapour phase sorp-:tion is the fact that one can assess the true affinity of the compound under study towards the adsorbent fibre. Most of the dyes and intermediates in which we are interested are compounds of high molecular weights and high melting points and it would be impossible to study them in their vapour phase without using temp-:eratures high enough to damage the fibres. But it is possible to choose simple benzenoid compounds with various functional groups which do vaporise below or about 110°C. Such a study might be of importance in the understanding of the chemistry of textile fibres.

It was with this intention that a comparative study of rates for wool and nylon (undrawn) was extended to higher temperatures. Three temperatures well above the melting point of phenol were chosen, viz. 60°, 70° and 80°C. The object was to calculate the heat of adsorption and the heat of activation.

Rate Studies from vapour phase

As in the case of aqueous phenol and aqueous benzoic acid, we could measure the zero point energy of activation by determining rates in the first few minutes of sorption, or we could calculate the velocity constants from the rate curves and then calculate the average energy of activation for the entire course of the reaction. We might also test the data by applying McBain's equation for solid solution (Eq. 6. p. 74) or Langmuir's equation of true adsorption (Eq 13 p. 76).

This has been done for the rate curves of phenol on undrawn nylon and wool. But unfortunately the experimental data obtained within the first 20 minutes were not very reliable and hence it was felt that it was not worth while to calculate the zero point energy. The reason for this seems to be due to an inherent difficulty in the experimental technique. We shall state in brief the experimental procedure.



HIGH TEMP. SORPTION APPARATUS.

Rate Studies from vapour phase

Above is a diagrammatic representation of the sorption tube.

Phenol was contained in the liquid bulb B and the fibre was hung by the spring S in the totally immersed sorption tube t. T is the thermostatic bath containing liquid paraffin. s_1 is a three way stopcock connecting the liquid bulb, the sorption tube and the vacuum line. The liquid bulb can be evacuated by suitably opening stopcock s_1 and closing s_2. s_2 is a T tap connecting the sorption tube to the vacuum line. The fibre alone could be evacuated by opening stopcock s_2 and closing s_1. When measurements of rate are to be made, s_2 is closed, and connection is made between the liquid bulb B and the sorption tube t by suitably opening s_1. The length of the spring s is measured from time to time by means of the cathetometer. It is felt that it is in such a procedure that the real difficulty lies. As soon as s_3 is opened, the vapour from the liquid bulb B will suddenly expand into the sorption tube t. This expansion will cause cooling and what is measured as sorption within the first few minutes may just be a condensation of the vapour on the fibre caused by the cooling due to expansion. It was not possible to improve this technique and avoid such an expansion of vapour. Hence the idea of measuring rates in the initial few minutes had to be given up.

To avoid this difficulty rate measurements were done for a long period (about 4 hrs.) so that there was ample time for the temperature of the sorption tube to become uniform.

Figs. 44 and 45 show these rate curves for wool and undrawn

nylon respectively. The data are given in Tables 34 to 39.

Firstly we note that at all the three higher temperatures, both wool and nylon show comparable rates. The slowness of the rate of sorption observed at 25°C is not evident. This seems remarkable. If we explained the slowness of sorption rate in wool as due to the resistance offered by the thin membrane sur-:rounding the woollen fibre, we must conclude that the membrane is ruptured at higher temperatures.

Secondly, the effect of temperature on the rate is not regu-:lar. Thus the curve at 70°C crosses the curve at 80°C in the case of both the fibres in a characteristic way. In the first hour, however, the rates do show a regular gradation. The rate curve at 70°C lies between the two curves at 60° and 80°C. It is difficult to offer any satisfactory explanation for such a peculiar behaviour.

It is likely that the effect of temperature on the activity of the phenol molecule itself is rather irregular. For example, the mechanism of the solution of phenol in water is yet not pro-:perly known. It is known that at 68·3°C (54A) phenol is miscible in water in all proportions. This is called the criti-:cal point. It may be remarked that our curves at 70°C (near the critical point) show the most rapid rate. But if the

activity of the phenol molecule is at its highest point at 70°C, why should it be lower at 80°C ? It is possible that at 80°C the rate of sorption is actually comparable with that at 70°C, but due to the increased temperature the rate of evaporation also increases and thus the curve at 80°C exhibits lower rates of sorption.

Since the curves cross each other, it is apparent that phenol does not have a uniform energy of activation for the entire range of temperatures. It would serve no useful purpose to calculate the energy of activation for the entire process. But the activation energy at the zero point could be calculated by drawing slopes to the rate curves and finding the values of the velocity constant as in the case of aqueous phenol. This has been done for the rate data of phenol vapour on nylon and wool. The activation energy for phenol on wool is thus found to be 6,500 cal/g. mol. and that for nylon 5,000 cal./g. mol. It is to be noted that the order of the activation energy is the same in both cases, but wool gives a slightly higher value. This means that the resistance offered to the phenol molecules is greater in the case of wool. If we assume that the sorption sites in both the fibres are similar (-NH-CO-groups) this added resistance in wool must again point to the correctness of Phillip's discovery (see p. 85) that the cuticular cells of wool are surrounded by an impervious or semi-pervious membrane.

Rate Studies from vapour phase (Contd.)

(iv) Acetic acid vapour on nylon and wool: Glacial acetic acid dried over sodium sulphate (anhydrous) was used.

Comparison between drawn and undrawn nylon: In Tables 40 and 41 are given the rate data at 25°C. Fig.46 shows the course of reaction within the first 40 mins. Fig.47 shows the overall rate within the first 250 mins. For both the fibres no tendency towards equilibrium is shown. As in the case of phenol the rate for drawn nylon is higher than that for undrawn nylon. Again, the increased surface area available in drawn nylon must be the reason.

In the vapour phase, one would expect that acetic acid is not ionised, so the mechanism of combination of acetic acid with nylon cannot be explained on the basis of salt formation. It is likely that the undissociated molecules of acetic acid combine with the NH-CO groups by hydrogen bond formation.

McBain's diffusion equation (p.74) was applied to the data of both drawn and undrawn nylon and as Fig.48 ↓ shows, the equation is obeyed in both cases. This is interesting; comparing with the data for water and the two alcohols (p.79), it appears that the behaviour of acetic acid on nylon is essentially similar in mechanism to that of water and the two alcohols. This would suggest a similarity in the hydrogen groups of all the four vapours. This is in support of the view, suggested elsewhere, that acetic acid might combine with nylon by hydrogen bonding at the -NH-CO groups.

↓ Fig. 48 follows after p. 96

Rate Studies from vapour phase

Rate of sorption of acetic acid vapour on wool

In one set of experiments the temperature of the liquid, the vapour and the fibre were identical. Rates were determined at four different temperatures, 30·0°, 40·5°, 50·5° and 60·5°. The data are given in Tables 42 to 45 and the rate curves at the four temperatures are shown in Fig. 49.

In another set of experiments, the temperature of the bulb holding the acetic acid was maintained constant and the temperature of sorption was varied. The data for these rates are given in Tables 46 to 48 and the rate curves are shown in Fig. 51. The reason for taking these two sets of readings was that in the first set of experiments, with the variation of temperature of the liquid bulb, its vapour pressure is also bound to vary. In this set therefore there would be two variables to contend with, viz., tem-:perature and pressure. In the latter case, however, since the temperature of the liquid bath was held constant, the vapour pres-:sure of the sorbate liquid would be constant and this would make the interpretation of the rate curves easier. We shall consider the two sets of data separately.

Sorbent and sorbate at the same temperature

A glance at Fig. 49 shows that the rate of sorption of acetic acid on wool increases with increasing temperature. In the figure the rate curves are only shown for the first 20 mins. But it was

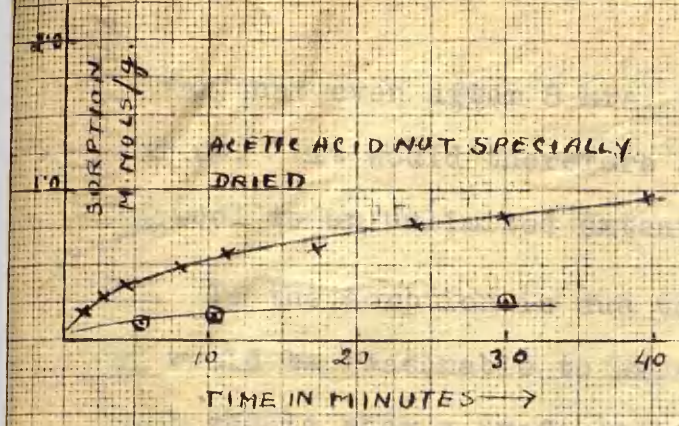


FIG. 46

RATE OF SORPTION OF ACETIC ACID VAPOUR ON DRAWN AND UNDRAWN NYLON AT 25°C. WITHIN THE FIRST FEW MINUTES.

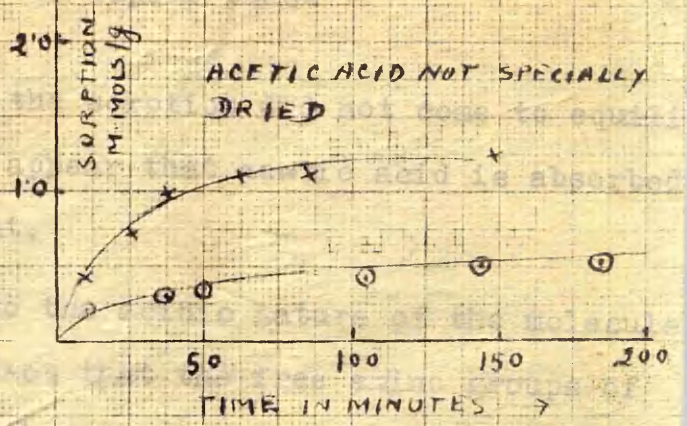


FIG. 47

RATE OF SORPTION OF ACETIC ACID VAPOUR ON DRAWN AND UNDRAWN NYLON. : OVERALL RATE.

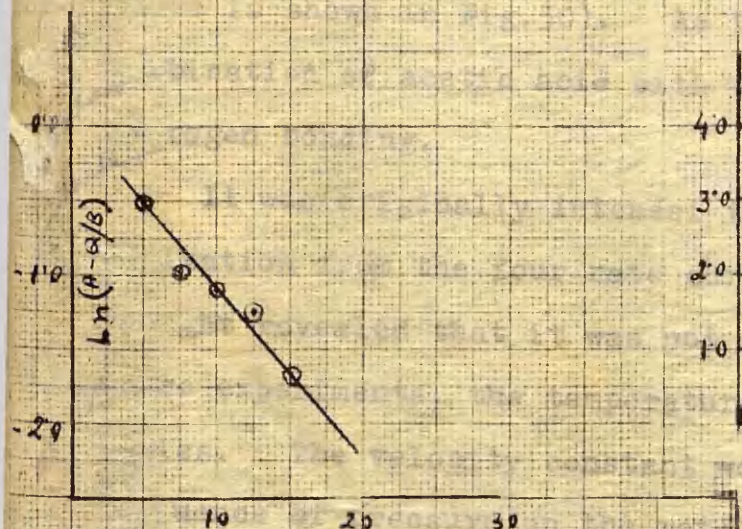


FIG. 50

McBAIN'S DIFFUSION EQUATION APPLIED TO DATA OF ACETIC ACID SORPTION ON WOOL.

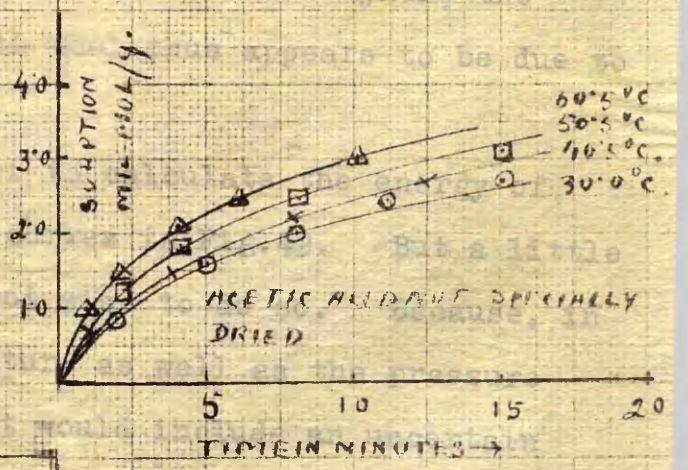


FIG. 49.

EFFECT OF TEMPERATURE ON THE RATE OF SORPTION OF ACETIC ACID VAPOUR ON WOOL

found that even after 8 hrs. the sorption did not come to equili-:brium. It would therefore appear that acetic acid is absorbed by wool to an unlimited extent.

If the sorption is due to the acidic nature of the molecules, it would be reasonable to expect that the free amino groups of wool should show a preferential rate. Since the sorption value is found to be far greater than 0.85 m.mol/g. it is also quite evident that it is not restricted to the more basic amino groups in the fibre.

McBain's equation for diffusion was applied to the curves in Fig.49. Here again the equation was obeyed. (Only one such curve is shown in Fig.50). As in the case of nylon, the combination of acetic acid with wool thus appears to be due to hydrogen bonding.

It was originally intended to calculate the energy of activation from the four rate curves in Fig.49. But a little thought revealed that it was not wise to do so. Because, in these experiments, the temperature as well as the pressure varies. The velocity constant would include an uncertain influence of pressure on the rate and hence the values for the temperature coefficients would be unreliable.

Even so, for each rate curve, under isothermal conditions, a

correction for the pressure effect could be applied. Obviously, the higher the pressure, the greater the rate. Hence, the rate $\frac{dx}{dt}$ is given by

$$\frac{dx}{dt} = k. \; p_{(T)} \qquad \ldots\ldots\ldots\

mean that the activation energy for acetic acid on wool is negli-:gibly small. But such results are not uncommon. Thus, Barrer and Rideal (68A) found that for the rates of adsorption of hydro-:gen, oxygen and nitrogen on sugar carbon, the temperature coeffi-:cients are negligible.

There is, however, one other possibility. The acetic acid used by us was not specially treated to remove all traces of mois-:ture. If the heat of sorption for water is negative and that for acetic acid is positive, the two opposite heat effects might nullify the resultant heat. Hence the rate experiments were re-:peated with a specially stabilised and dry acetic acid. The method of purification was as follows:-

"Analar" acetic acid was refluxed with 6 g/l. pure chromic anhydride (CrO_3) and then fractionally distilled. The fraction boiling at 117·5 to 118·5°C was collected in a flask connected to a drying tube filled with calcium chloride.

The effect of varying pressures was also remedied by placing the bulb containing the acid in an air thermostat. The sorption tube was immersed in a water bath. The temperature of the air thermostat was 28°C throughout. Three rate curves were deter-:mined, at 30°C, 35°C and 45°C. The data are given in Tables 46-48, and the rate curves are shown in Fig. 51.

Rate Studies from vapour phase

Comparing with Fig. 49, it will be noted that the rate is very much slower. Furthermore, the rates within the first five minutes show an increase with temperature, but as time proceeds, the rate becomes slower with temperature. The curves cross each other and the curve for 45^{o} takes the lowermost position. It is quite evident therefore that even traces of moisture affect the course of reaction of acetic acid on wool. But, the fact that dry acetic acid has an appreciable sorption on wool is significant. The process of its combination must be non-ionic. Possibly it combines with wool by hydrogen bonds.

The zero point activation energy has been calculated and it is interesting to note that its value is 4,700 cal/mol. which is very slightly smaller than that for phenol (see p. 90). That the magnitude of the activation energy for both phenol and acetic acid on wool is alike, is, it is felt, another pointer that the nature of binding of acetic acid and phenol with wool is essentially similar. Hydrogen bond formation can explain their mode of combination equally well.

Desorption rates for acetic acid on wool

As in previous cases, the desorption was done by continuously evacuating the contents of the sorption tube and measuring the spiral length from time to time. Table 49 gives the data. In

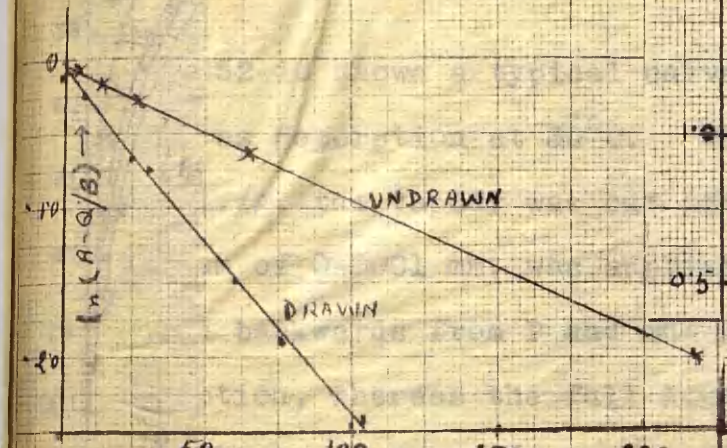


FIG. 48

MC BAIN'S DIFFUSION EQUATION TO DATA OF FIG 47

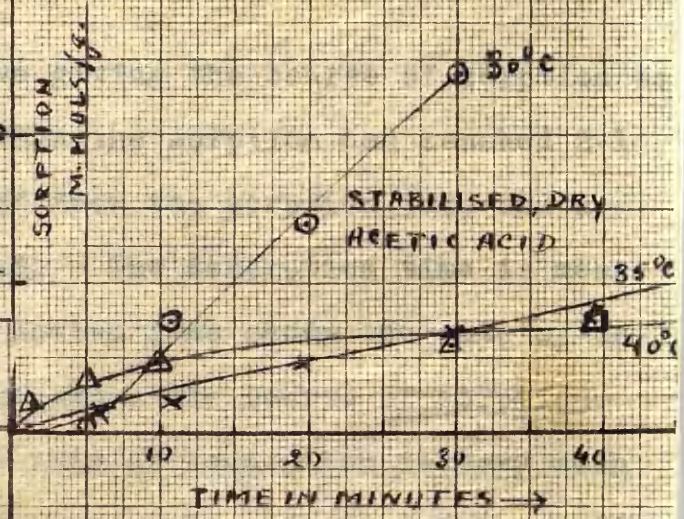


FIG. 51.

EFFECT OF TEMPERATURE ON THE RATE OF SORPTION OF STABILISED DRY ACETIC ACID ON WOOL.

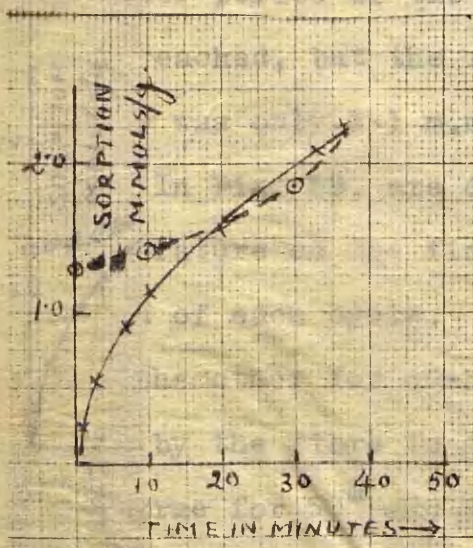


FIG. 52.

RATES OF SORPTION AND DESORPTION OF ACETIC ACID VAPOUR ON DRAWN NYLON AT 30°C.

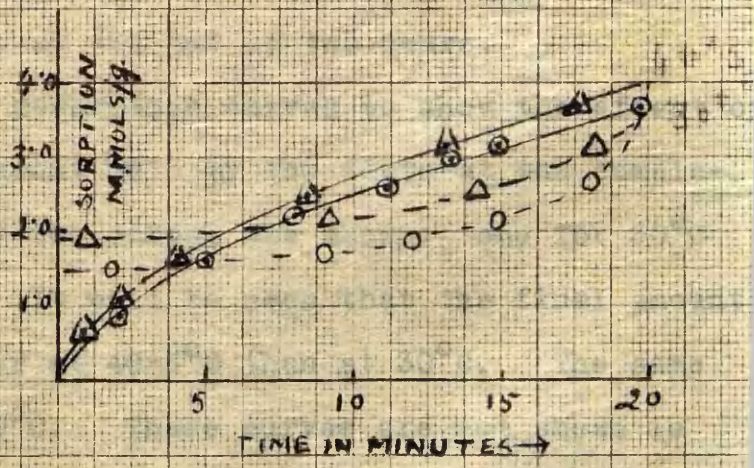


FIG. 53.

RATES OF SORPTION AND DESORPTION OF ACETIC ACID VAPOUR ON WOOL AT 30°C AND 40·5°C.

Rate Studies from vapour phase

Fig. 52 is shown a typical curve giving the course of sorption as well as desorption at 30°C. When the sorption had reached 2·1 m.mol./g. the vapour was cut off from the sorption tube and a vacuum of 0·0001 mm. was applied. The desorption time is measured backwards from P and the dotted line shows the rate of desorption, whereas the full line shows the course of sorption.

It is to be noted that the rate of desorption is very much slower. At the end of the complete cycle (33 mins. for sorption and 33 mins. desorption) out of a total quantity of 2·1 m.mol/g., 1·25 m.mol/g. is still left on the fibre. To determine if any limiting value was reached, the desorption was continued for a further period of two hours. It was found that no limiting value was reached, but the rate of desorption was extremely slow. The value was only 1·1 m.mol/g. at the end of two hours.

In Fig. 53, are drawn desorption curves to show the effect of temperature on the final amount held by the fibre at the completion of each cycle. Only two curves are shown; one for 30°C and the other for 40·5°C. It will be seen that the final amount held by the fibre is greater at 40·5°C than at 30°C. The same was true for 50° and for 60°C. These curves are not shown in the figure.

Here again if the acetic acid is held by the free amino

groups in wool in some preferential manner, one would expect the curves to show a comparative ease of desorption above values of 0·85 m.mol/g. of absorbed acetic acid. The absence of any such ease in desorption is taken to mean that, whatever may be the mechanism, the acetic acid molecules do not form salt linkages with the basic side chains of wool.

Comparison of the action of acetic acid and hydrochloric acid on wool

It is generally well known that weak organic acids are taken up by the wool fibre in far greater amounts from aqueous solution than are the strongly ionising acids such as hydrochloric or sul-:phuric acid. It is easy to study hydrochloric acid vapour and a rate study was therefore made with it.

For this purpose dry hydrogen chloride was prepared inside the sorption apparatus itself. "Analar" sodium chloride was placed in the bulb and sulphuric acid contained in a thin walled sealed glass phial was held in position over it. The bulb carry-:ing the two substances was then attached to the sorption appar-:atus and evacuated to remove all air. After evacuation, the acid phial was broken by moving a piece of iron held in a glass cover magnetically and allowing it to fall upon the phial. Dry hydrogen chloride was generated. A suitable quantity of this gas

was then taken up in the sorption apparatus. Actually the pressure of the gas could be adjusted to any desired amount by collecting a controlled quantity of vapour inside the apparatus. The degassing was done in the usual manner.

The pressure at which the gas was studied was 78 mm. As Table 50 shows, the amount of hydrochloric acid held by the fibre is negligible. Whatever little amount is taken may be due to surface forces or to the very small amount of moisture that might have been left undegassed from the fibre. Increasing the pressure of the hydrochloric acid gas did not make any change in sorption. It must therefore be concluded that dry hydrochloric acid gas is not sorbed by wool fibre. It is a well known property of hydrochloric acid that it does not ionise in the absence of moisture, and unionised acid can not form salts with basic amino groups. It seems likely therefore that there is a very fundamental difference in the action of acetic acid and hydrochloric acid on wool.

Speakman and Scott (12) measured the heats of reaction for aqueous hydrochloric acid and aqueous chloracetic acid on wool. They found that the heat of reaction for hydrochloric acid remains nearly constant both with respect to the p_H of the bath and the amount of acid taken by the fibre. The average value was about 3·6 k.cal. per g.mol. of acid held. For chloracetic acid, however,

the heat of reaction decreased with the amount of acid held. The lower limit was 2·29 and the highest value was 3·76 k.cal.per g.mol. The following Table gives a summary of their results.

TABLE 51

Heats of reaction for hydrochloric acid on wool
(Speakman and Scott)

Hydrochloric acid				Chloracetic acid			
Final p_H	c.c.of N/1 Acid/loog Wool	Δ H k.cal/g mol.	ΔH k.cal. per 1250 g. wool	Final p_H	c.c.of N/1 Acid/100g. Wool	ΔH k.cal/g. mol.	ΔH k.cal. per 1250 g.wool
2.52	27.5	3.96	1.36	2.64	22.6	3.76	1.06
1.99	53.0	3.43	2.29	2.35	36.0	3.09	1.39
1.82	61.0	3.74	2.86	2.13	51.0	3.03	1.93
1.48	73.0	3.42	3.12	2.08	55.0	3.36	2.31
0.79	80.0	3.65	3.65	1.44	82.3	2.46	2.52
				1.25	153.0	2.29	4.38
				0.88	-	-	7.26

It will be noted from the above Table that the authors express heats of reaction both as k.cal. per g.mol. of acid and as k.cal. per 1250 g. of wool. The heat of reaction expressed as k.cal./g.mol. for hydrochloric acid remains constant with increasing quantity of acid held. It shows a slight decrease for chloracetic acid when expressed similarly.

It appears from their paper that the authors do not attach any great significance to this fact. On the other hand, they

calculate the heats for a quantity they term the gram-equivalent wt. of wool (1250 g.) and show that when so calculated the heat of reaction gradually increases with increasing quantity of acid held in both cases. For hydrochloric acid it ranges from 0.79 to 3.65 k.cal./g.mol. and for chloracetic acid, from 1.06 to 9.17 k.cal./g.mol.

It is customary to express heats of reaction in terms of a g.mol. of the adsorbate. The reason why these authors attach more importance to the gm. equivalent weight of wool may be that they assume the combination of both the acids to be by salt formation at the amino groups. But, if so, it would be difficult to explain the data of our rate measurements for acetic acid and hydrochloric acid vapours. Unionised hydrochloric acid gas does not combine with the wool fibre. If the mechanism of attachment of the acetic acid molecule was similar to that of the hydrochloric acid molecule, i.e. if it were an ionic combination, we should have expected dry acetic acid vapour not to combine with wool. But our experimental results show that it does. It is quite likely that acetic acid combines with wool by hydrogen bonding in a manner similar to its combination with nylon. Its low heat values in such a case would not be surprising. In fact our rate curves indicate that its sorption on wool has a very low temperature

coefficient. This indicates that combination of acids with wool is after all not as simple as it is usually supposed to be.

II C. Rate Studies from vapour phase (contd)

(v) Sorption of vapours of β-naphthol and alizarine on wool and nylon

β-naphthol melts at about 118°C and alizarine at 290°C. Very much higher temperatures are therefore needed for their vapour phase study. It is generally believed that wool is decomposed when heated to temperatures higher than 110°C. Below this temperature the vapour pressures of both alizarine and -naphthol are so small that there is no appreciable sorption. Hence it became apparent that temperatures higher than 110°C. must be used for the sorption study. It was therefore necessary to see if heating under vacuum up to say 150°C would cause any damage to the fibre. We do not know what actually happens to the wool fibre when it is subjected to heat. But it was decided that if there was no loss in weight due to heating, we should assume that the fibre does not appreciably decompose.

An experiment was therefore done in which 0.1 g. of wool or nylon was hung on a glass spiral mounted in the sorption tube. The contents of the tube were evacuated and the tube was heated to 120° or 150°C. for 8 hrs. It was observed that there was a loss in weight corresponding to about 3.5 to 4.2% in nylon and about 10 to 12% in wool within the first one hour. After that the weight remained constant. Thus, the action of heat at high temperature

only removes the moisture and probably traces of other adsorbed impurities, but does not seem to decompose the fibres.

Sorption of β-naphthol on nylon and wool

Drawn nylon, undrawn nylon, powdered nylon (prepared as described on p.59) and wool were studied. The Tables 52 to 55 give the data for the rates at 120°C and Fig. 54 shows the rate curves for the four fibres. It is to be noted that, as in the case of phenol, wool again shows a very slow rate of sorption as compared to the three varieties of nylon. Curve 1 shows the rate for wool. Curves II, III and IV show them for undrawn, drawn and powdered nylon respectively. Among the three varieties of nylon, the effect of available surface area on the sorption is very clearly shown by the rate curves. Thus, undrawn nylon, with the least amount of exposed surface, shows the slowest rate, whereas powdered nylon with a very high surface area, shows the highest rate.

It is to be recalled that a comparison of the rate curves was made for drawn and undrawn nylon in the case of phenol and acetic acid. In both cases, the drawn fibre showed a higher rate of sorption. We explained the results by saying that the higher rate was due to the higher surface area in the drawn fibre. The extension of the results to powdered nylon in this case seems

to confirm our previous conclusion. In other words, there seems to be no specificity in the combination of phenol or β-naphthol or acetic acid as far as reactive groups in nylon are concerned. All the three compounds seem to combine by a similar mechanism (presumably by hydrogen bonding at the -NH-CO- groups). The so-called "crystalline" or "amorphous" regions also do not seem to have any directing influence on the adsorbate molecules.

Energy of activation of β-naphthol for wool and nylon

In the case of wool, rates were measured at 120°C and 130°C. Only powdered nylon was studied at three temperatures, 120°, 133° and 140°.

Tables 55 to 58 give the data.

In Fig. 55, the two rate curves at 120° and 130°C for wool are drawn. By drawing slopes to the rate curves at the zero point, the energy of activation for β-naphthol on wool is calculated. The value so found was 7,400 cal./g.mol.

Similarly the three rate curves for nylon at 120°, 133° and 140°C are shown in Fig. 56. It is rather remarkable that the curve at 120°C takes a middle position with respect to those at 133° and 140°C. It is difficult to explain why this should be so. We have neglected this curve for the calculation of the activation energy. The activation energy for the combination of β-naphthol

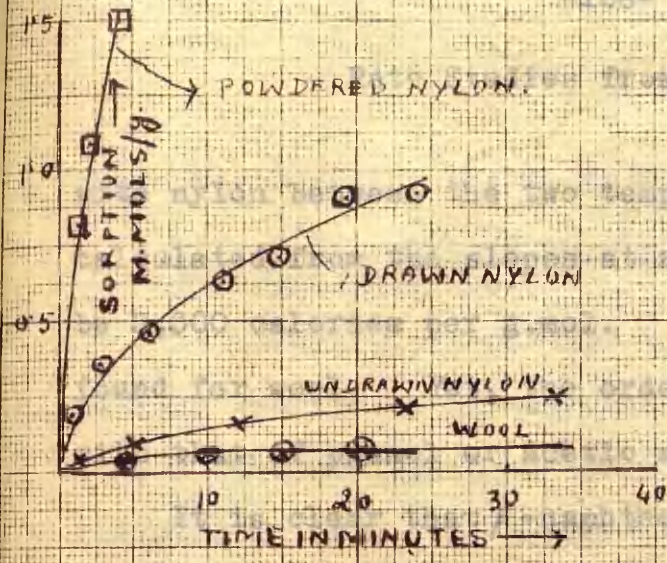


FIG. 54.

RATE OF SORPTION OF β-NAPHTHOL VAPOUR ON NYLON AND WOOL AT 120°C.

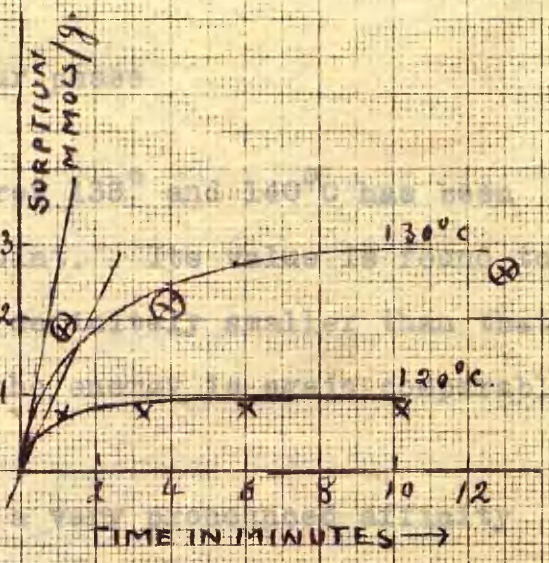


FIG. 55.

EFFECT OF TEMPERATURE ON THE RATE OF SORPTION OF β-NAPHTHOL VAPOUR ON WOOL.

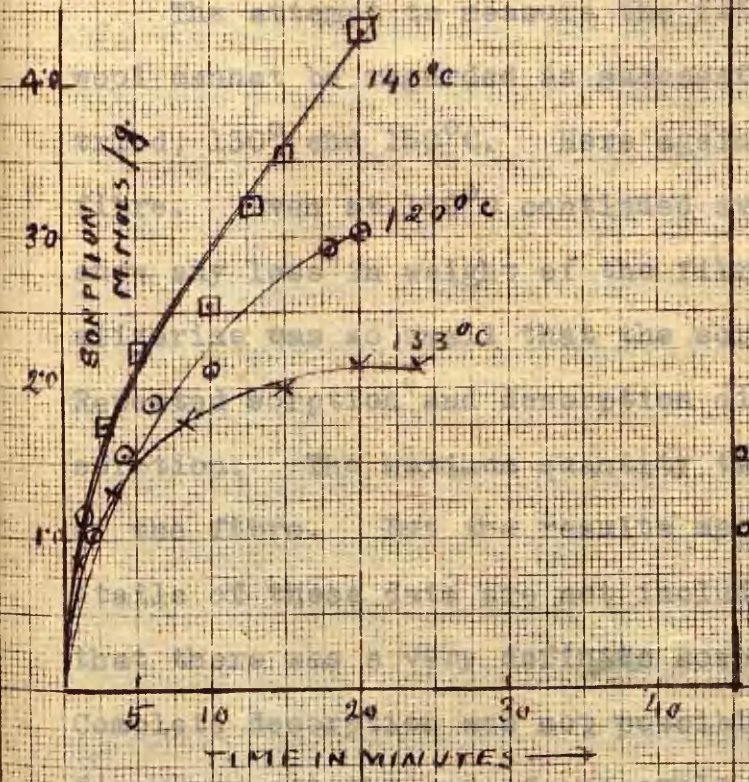


FIG. 56.

EFFECT OF TEMPERATURE ON THE RATE OF SORPTION OF β-NAPHTHOL ON POWDERED NYLON.

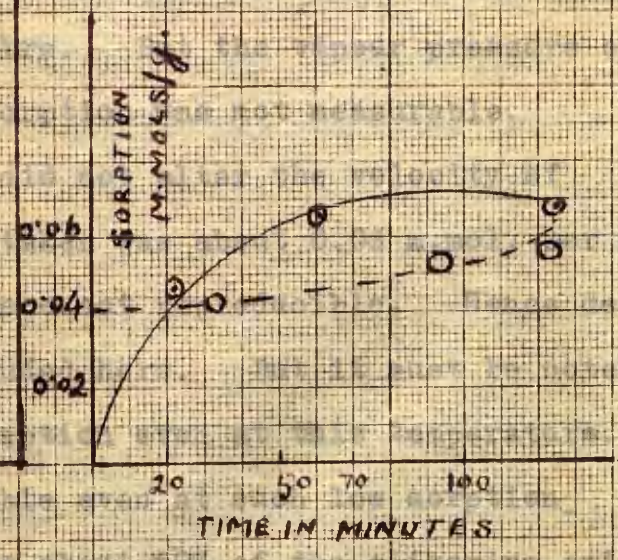


FIG. 57.

RATE OF SORPTION AND DESORPTION OF ALIZARINE VAPOUR ON WOOL.

with nylon between the two temperatures 133° and 140°C has been calculated from the slopes at zero point. Its value is found to be 5,300 calories per g.mol. It is definitely smaller than that found for wool. Yet, the order of the energy is again comparable with that of phenol or acetic acid.

It is clear that β-naphthol has a very pronounced affinity for both nylon and wool and from the rate curves there is no indi-:cation of any selective action on the free amino groups in wool.

Rate of sorption of alizarine on wool.

The attempt to measure the rate of sorption of alizarine on wool cannot be regarded as successful. Two temperatures were tried, 130° and 150°C. Here again heating did not decompose the fibre. Even at 150°C continued evacuation for 3 hrs. did not show any loss in weight of the fibre. But the vapour pressure of alizarine was so small that the sorption was not measurable. Repeated sorption and desorption did not alter the velocity of sorption. The maximum quantity taken was about 0.06 m.mol. per g. of the fibre. But the results were not reproducible. Hence de-:tails of these data are not included here. But it must be noted that there was a very definite sorption even at this temperature. Complete desorption was not possible even at such low sorption figures. At the end of one cycle about 50% of the alizarine ori-:ginally held by the fibre is still retained by it. A typical

curve for sorption and desorption at 130° is reproduced in Fig.57.

Effect of repeated sorption and desorption of β-naphthol on nylon and wool

It became apparent that the rate of reaction of β-naphthol depends greatly on the way the fibre is treated before sorption. It was therefore decided to study this aspect a little more systematically. For this purpose the fibre was degassed at high vacuum at the temperature of the experiment and sorption was allowed to take place for a known length of time. Since no equilibrium was reached, the forward process was stopped by cutting off the vapour and then the sorbent was subjected to evacuation at the same vacuum as used for original degassing. The desorption was continued for exactly the same length of time. When one full cycle was thus completed, the fibre was again exposed to the vapour and sorption was measured for the second time. After a time, sorption was stopped and desorption started again and the second cycle was thus completed. Tables 59 to 62 give the data for the three varieties of nylon (drawn, undrawn and powder) and wool.

Fig. 58 shows one full sorption desorption cycle for drawn nylon lasting for 24 mins. in the forward reaction and for the same period in the backward reaction. It will be noticed that complete desorption was not possible and that about 0.75 m.mol/g. of the β-naphthol was retained by the fibre at the end of the

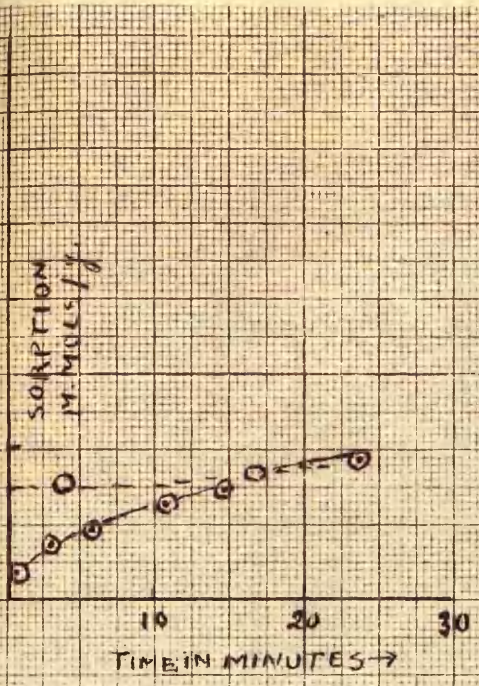


FIG. 58

RATES OF SORPTION AND DESORPTION OF β-NAPHTHOL VAPOUR ON DRAWN NYLON AT 120°C

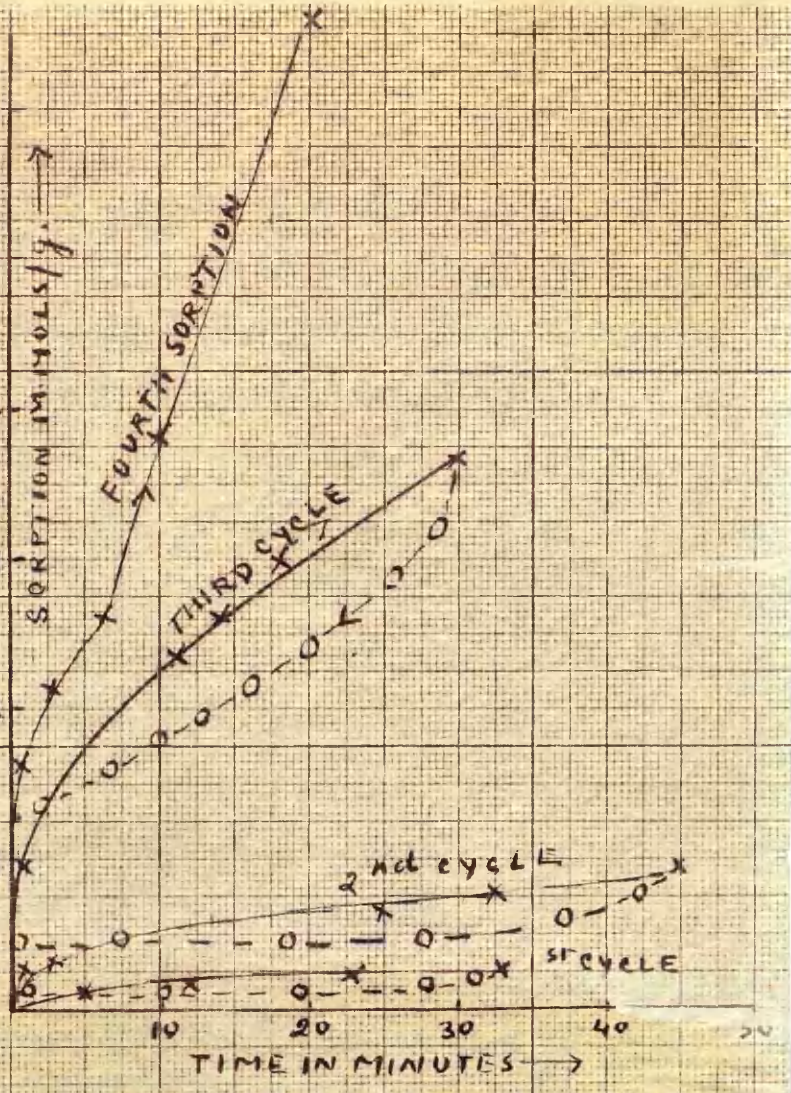


FIG. 59. RATES OF SORPTION AND DESORPTION OF β-NAPHTHOL ON UNDRAWN NYLON AT 120°C

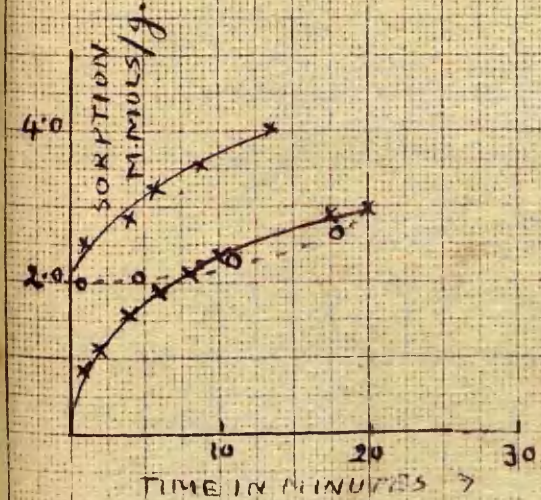


FIG. 60

RATES OF SORPTION AND DESORPTION OF β-NAPHTHOL ON POWDERED NYLON

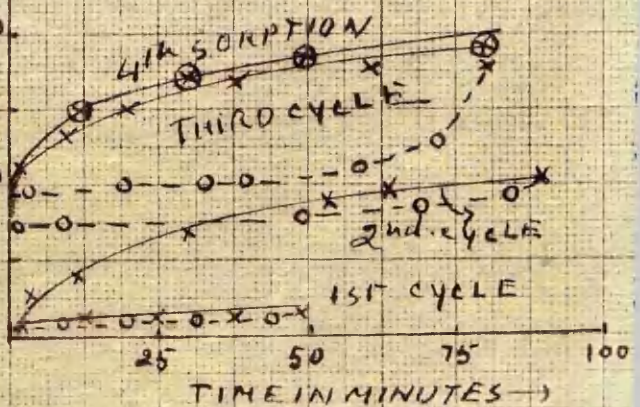


FIG 61

RATES OF SORPTION AND DESORPTION OF β-NAPHTHOL ON NYLON AT

cycle. The temperature of the bath was maintained at 120°C throughout. The dotted line represents the desorption curve and the full line the sorption curve.

In Fig. 59 three such full cycles are shown for undrawn nylon. It is very interesting to note that after each successive sorption and desorption, the rate of sorption shows a considerable rise. This is very clearly seen in the curves. Thus in the first sorp-:tion hardly 0.25 millimole are taken up within 34 mins. Out of this only about 0.15 m.mol/g. is desorbed in the first desorption. In the second sorption, however, as much as 0.75 m.mol/g. is taken up in 34 mins. Of this 0.55 m.mol. is retained at the end of the desorption cycle. In the third cycle these values rise still higher: the sorption value rises to 3.7 m.mol. in 30 mins. and the amount held at the end of the third cycle is 1.25 m.mol/g. In the fourth sorption, remarkably enough, there is a distinct breakpoint in the rate curve at about 2.75 m.mol/g.

In Fig. 60 are shown sorption and desorption curves for nylon powder and a similar tendency is observed.

In Fig. 61 are shown again three complete cycles of sorption and desorption for wool, and the data are included in Table 62. It is interesting to note that wool also shows an exactly similar tendency. The quantitative aspects of the amounts held at the

end of each cycle are not discussed. No parallel results have been found in the literature. It is felt that our own results do not allow us to draw any far reaching conclusions. It appears, however, that somehow at the end of each successive cycle, the fibre becomes more receptive and this causes an appreciable in-:crease in the rate of reaction. How does this happen? There is one possibility. The adsorbed molecules of β-naphthol might be free to move inside the fibre. In so doing they might open up the lateral hydrogen-bonds in the peptide chains and expose a greater number of sorption-centres. One thing, however, is made clear. The surface of the fibre cannot be treated as a rigid surface with a fixed number of sorption centres. Depending on the nature of the adsorbate molecules, it has a tendency to break up from within. When this happens, all classical theories of sorption which are built up on the assumption of a "free" and "constant" surface be-:come inadequate to explain the sorption data.

II C. Rate Studies from vapour phase (contd)

(vi) Benzoic acid vapour on nylon and wool

Rate of sorption of benzoic acid on powdered nylon and wool

Benzoic acid melts at 121°C. Its sorption has been studied on nylon and wool at one temperature only. The idea was to compare its action with acetic acid. The molecular size of benzoic acid is greater than that of acetic acid. Its dissociation constant (6.8×10^{-5}) is about four times as high as that of acetic acid (1.8×10^{-5}). A comparison of the rates of these two acids on nylon and wool would probably throw more light on the nature of combination of these two compounds.

Fig. 62 shows two complete cycles of sorption and desorption on powdered nylon. The data are given in Table 63.

There are two very striking features. Firstly, complete desorption is possible in this case. Secondly, in the second sorption, a maximum value of about 1.6 m.mol./g. of fibre is reached and then this spontaneously decreases with time. This is very puzzling and no explanation is given here. The results were checked two or three times. It is only to be noted here that this is rather an unusual behaviour and needs to be further investigated, but the tendency to reach a maximum and then decrease was still apparent.

In Table 64 are given data for the rates of sorption and

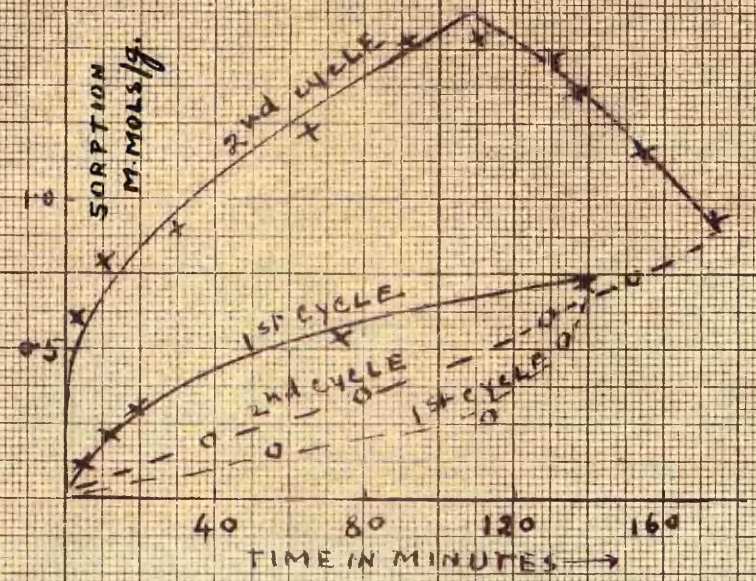


FIG. 62.

RATES OF SORPTION AND DESORPTION OF BENZOIC ACID ON POWDERED NYLON AT 130°C.

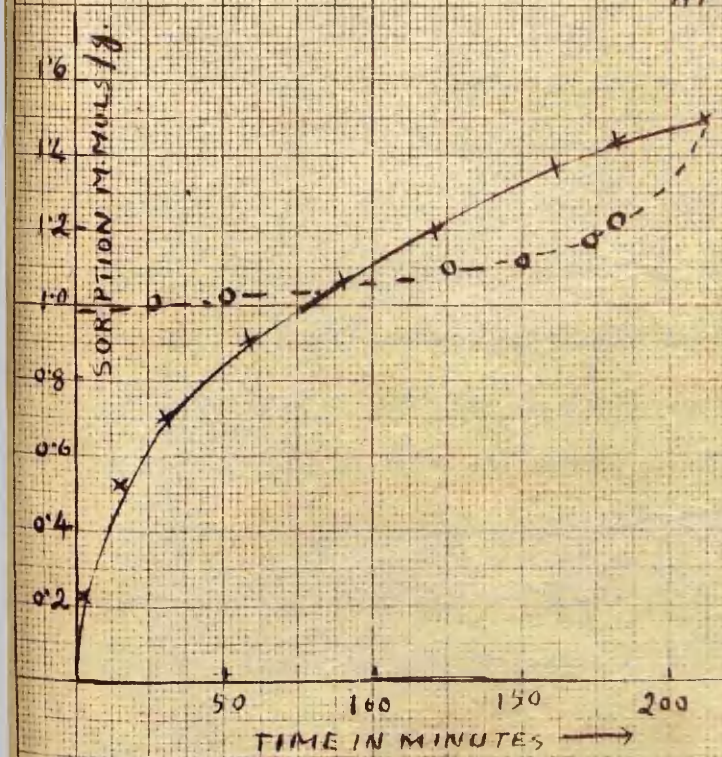


FIG. 63.

RATE OF SORPTION AND DESORPTION OF BENZOIC ACID VAPOUR ON WOOL

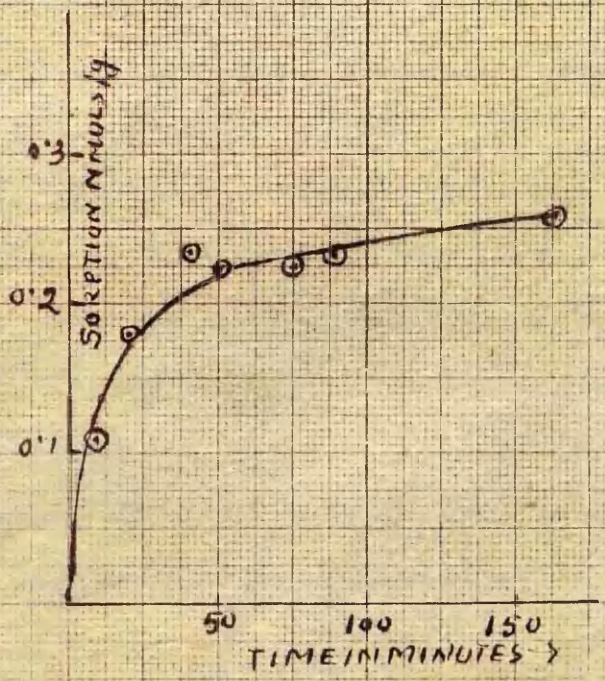


FIG. 64.

RATE OF SORPTION OF ANILINE VAPOUR ON UNDRAWN NYLON

Rate Studies from vapour phase

desorption of benzoic acid on wool. In Fig. 63, curves are shown to represent them. Again no equilibrium was reached. Unlike nylon, the desorption does not go to completion. In this connection a similarity with the behaviour of acetic acid is clearly seen. Round about the value of 1 m.mol./g. held, the rate of desorption becomes extremely slow.

It is interesting to note that β-naphthol, which is far less acidic in nature, is more difficult to desorb (see Figs. 61 and 63) than is benzoic acid.

Here again it is not possible to attach any great value to the quantitative aspects of sorption and desorption. For acetic acid, the amount held at the end of one cycle was, as we have seen (Fig. 52), 1.25 m.mol./g. or 1.75 or 1.95 m.mol./g. (Fig. 53) depending on the temperature of the experiment. In benzoic acid, at 130°C, and with the particular times of sorption and desorption used, the final amount held by the fibre at the end of one cycle is about 1.0 m.mol./g. It was at first thought that the number of free amino groups in wool (0.85 m.mol./g.) might be responsible for the quantities of acids so held. The fact that benzoic acid is completely desorbed from nylon, and not from wool, rather significantly pointed to such a possibility. But, as we have seen above, there is no fixed limit to the final amount of acid held

by the fibre at the end of any one cycle of sorption and desorp-:tion. Whatever else the reason, we can not therefore say that the amino groups in wool are primarily responsible for such a be-:haviour.

Why, in the case of benzoic acid the sorption should reach a maximum and then fall again, cannot be explained.

II C. Rate Studies from vapour phase (contd)

(vii) Rate of sorption of aniline vapour on drawn nylon

On pp. 36-37 we discussed the behaviour of aqueous aniline on nylon. We found that aniline was appreciably sorbed by the fibre. We also found that the isotherm did not show any tendency to reach a limiting value of sorption with increasing relative concentration of aniline in the sorption bath. We also suggested that aniline combines with the -NH-CO- groups in nylon by hydrogen bonding at the carbonyl oxygen. Its vapour phase study was undertaken to see if the assumption could be confirmed.

Rates of sorption of aniline at two temperatures were studied. Table 65 gives the data. Fig. 64 shows the rate curves. It is to be noted that aniline is not adsorbed at 25°C. At 70°C, however, a slight adsorption took place. The quantity adsorbed in 50 mins. was only about 0.1 m.mol./g. It was at first thought that the absence of any sorption at 25°C. might be due to the very low vapour pressure of aniline at that temperature. But, even at 70°C., it is seen that the sorption is almost negligible. The small degree of sorption might be due to van der Waals surface forces and might not indicate any specificity. We therefore conclude that in the vapour phase, the molecules of aniline cannot attach themselves to the carbonyl oxygen of the -NH-CO- group.

This is understandable. For, it is well known that the -NH-CO- groups in nylon are already involved in hydrogen bond formation and since a similar type of bond is to be formed by the incoming aniline molecule, it cannot have the excess energy to break the existing ones. But how then could we explain the appreciable amount of sorption observed from the aqueous phase? The same ar-:guments could be advanced and we can argue that we should not ex-:pect any appreciable sorption of aqueous aniline by nylon.

There is one possibility. In the aqueous solution, water molecules might be first adsorbed by the fibre and aniline mole-:cules might then be held by hydrogen bonding on top of these mole-:cules. The adsorption observed in the aqueous phase may not be true adsorption on nylon.

Since the above observation was made, some very interesting confirmation of this view has been provided by the recent work of Mehta/in (68B) this laboratory. While studying the adsorption of azo-:benzene on anodised aluminium, he observed that the latter cannot take up this compound from benzene solution but readily does so from aqueous-alcoholic solution. The explanation offered by him also supports the view that a direct attachment of the weakly hydrogen-bonding azo-nitrogen to the hydrogen in the hydrate of the aluminium oxide is not possible, because the hydrogen atom

inside the hydrate is already involved in linkage with oxygen by hydrogen-bonding. In the presence of water molecules, however, the azobenzene attaches itself on to a layer of water molecules already adsorbed.

II C. Rate Studies from vapour phase (Contd)

(viii) Rate of sorption of acetic acid vapour on wool variously treated

Three varieties of wool were used in this work.

I. Untreated wool: This was the same as was used for the study of the different vapours reported so far.

II. Wool treated with sulphuric acid: 1 g. of wool was boiled under a reflux for six hours in 200 c.c. of sulphuric acid solution at a p_H of 1.28. It was then washed thrice in distilled water and extracted thrice with 50 c.c. lots of a 25% solution of pyridine, to remove last traces of sulphuric acid. It was finally washed again several times in distilled water, steeped over night in a large volume of distilled water, squeezed and dried at 60°C and conditioned for 48 hours at room temperature.

III. Wool heavily dyed with Solway Blue B.S. 1 g. of wool was dyed for six hours at the boil with 200 c.c. of solution containing 7.5 g./litre of Solway Blue B.S. and enough sulphuric acid to bring the p_H to 1.28. It was thus assured that the acidity condition was identical with that of sample II above. After the dyeing was over, the sample was rinsed thrice with 500 c.c. of cold distilled water, squeezed and dried. Under these conditions, the fibre is very heavily dyed. It takes up dye far in excess of the quantity required to saturate all the amino groups of the wool fibre (25).

Rate Studies from vapour phase

The idea of studying the rate of sorption of acetic acid on these three samples was to see the effect of dyeing on this rate of sorption.

The acetic acid used was stabilised dry acetic acid specially prepared as described on p. 95.

Table 66 gives the rate data. Fig. 65 shows the rate curves for the three samples of wool. Curve 1 represents the rate for the untreated sample, Curve 2 the rate for the acid-treated sample, and Curve 3 for the dyed one. The temperature of sorption was 35°C in all cases. The liquid bath was held at 28°C.

It is very interesting to note that whereas the dyed sample shows an extremely low rate of sorption as compared to the un-:treated one, the acid-treated sample shows a considerably higher rate.

There are two possibilities to be discussed here.

(i) The sites to which the dye molecules are fixed, and those on which the acetic acid molecules are fixed might be simi-:lar. In such a case, all or most such sites would be occupied in the dyed fibre and hence the rate of sorption would be extreme-:ly slow. Or

(ii) The pores in the heavily dyed fibre might be blocked

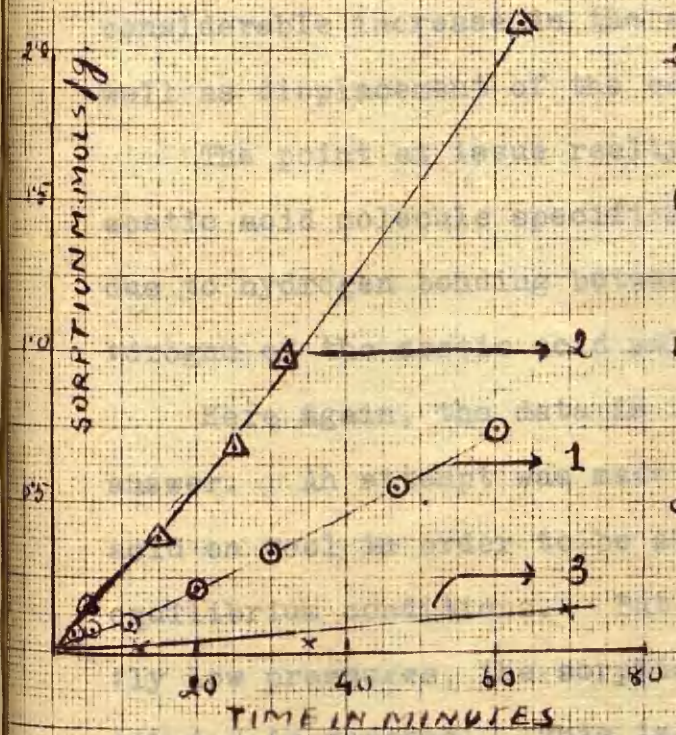


FIG. 65

RATE OF SORPTION OF ACETIC ACID VAPOUR ON TREATED WOOL AT 35°C.
1 = UNTREATED. 2 = ACID TREATED
3 = DYED.

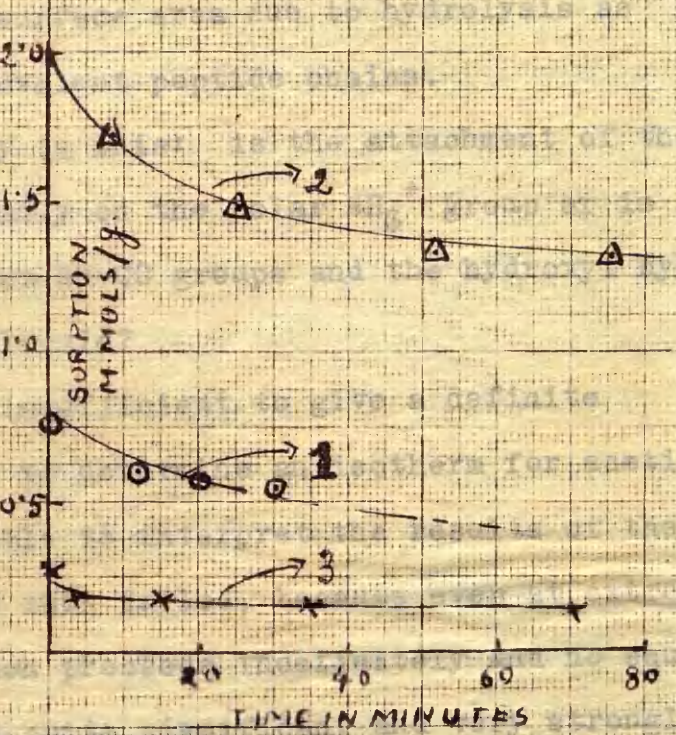


FIG. 65A.

RATE OF DESORPTION FROM TREATED WOOL; ACETIC ACID VAPOUR AT 35°C.

mechanically due to aggregation of the dye molecules and thus the low rate might be due to the difficulty of diffusion.

In the fibre treated with sulphuric acid alone, there is a considerable increase in the surface area due to hydrolysis as well as displacement of the covalent peptide chains.

The point at issue really is this: is the attachment of the acetic acid molecule specifically on the polar NH_3^+ group or is it due to hydrogen bonding between NH-CO groups and the hydroxyl hydrogen of the acetic acid molecule?

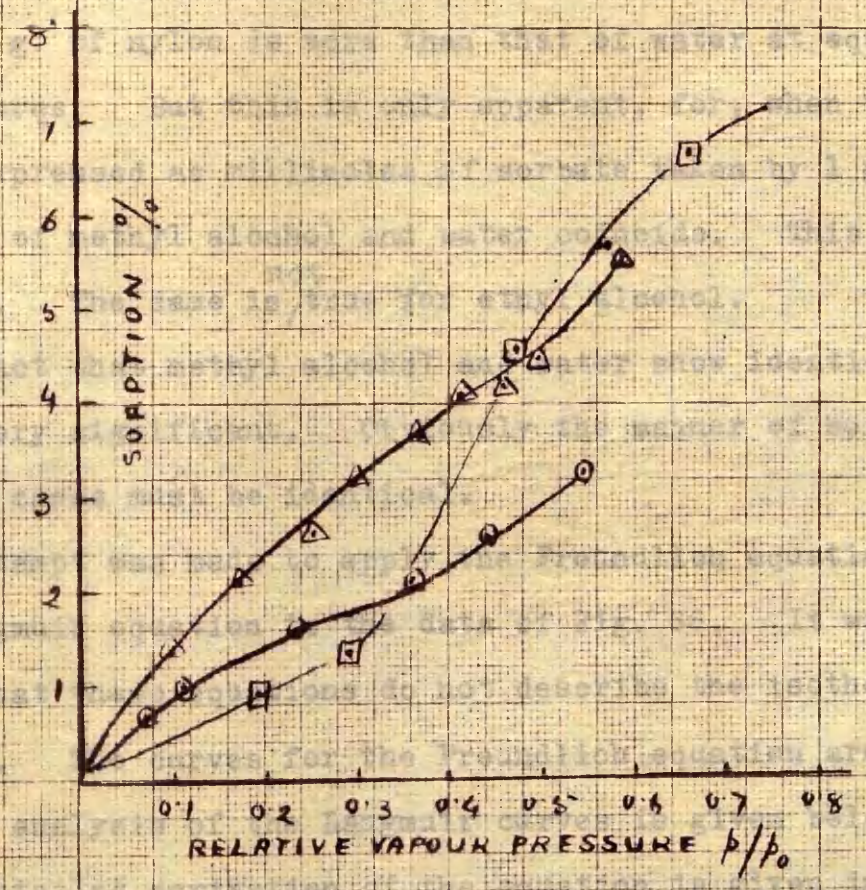
Here again, the data is insufficient to give a definite answer. An attempt was made to determine an isotherm for acetic acid on wool in order to be able to interpret the results of the equilibrium conditions. But this failed, because even at extremely low pressures, the sorption proceeds indefinitely and no equilibrium is reached. This is quite significant and very strongly suggests that the polar NH^{3+} groups do not exert any specific attraction towards the acid molecule. For if they did, the acid-sorption will stop when all the NH_3^+ groups are so occupied.

It thus appears from our evidence that the sorption of acetic acid on wool is not ionic. Hydrogen bonding, as suggested above, might very well explain the behaviour of this acid towards wool.

In each case, desorption rates were studied and the curves

are shown in Fig. 65A (Table 67 gives the data). All the three desorption curves are typically similar, and in all cases complete desorption is not possible. But there is also no limiting value reached. The acid is slowly but continually desorbed. Further, as will be seen from the figure, the higher the initial quantity held, the greater is the final value held at any instant during desorption. This slow but gradual desorption in all the three samples would again suggest that there is no specificity of the amino groups in attracting the acid molecule.

It is thus clearly seen that the combination of wool with acetic acid is something essentially different from the combina-:tion of a base and an acid. Perhaps the habit of trying to ex-:plain the behaviour of wool with acids and acid dyes in general as a typical case of acid base combination may not be entirely correct. The ionised groups in the wool fibre may not play as important a part in its combination with acids or acid dyes, as they are supposed to do. In fact, one wonders if the acidic or basic groups in the wool fibre are not too weak to form salt like linkages. It appears to us that the theory of stoichiometric combination of wool towards acids or acid dyes is far too imper-:fect to be true. Other types of bonds - such as the hydrogen bond - might play a very important role in the combination of acids or acid dyes with wool.



● — ● = WATER ▲ — △ METHYL ALCOHOL

□ — ⊡ = ETHYL ALCOHOL

FIG. 66

ISOTHERMS FOR WATER, METHYL ALCOHOL AND ETHYL ALCOHOL ON DRAWN NYLON.

Rate Studies from vapour phase

(ix) Conclusions from vapour phase rate studies

The experiments described in the last eight sub-sections are a little scattered and disconnected; because they represent a new technique, that of study of rates of sorbtion of high-melting compounds such as benzoic acid and β-naphthol on fibres, in the vapour phase. It is also felt that in all cases where the sor-:bate and sorbent were held at the same temperature, the experi-:mental technique itself needs some improvement. As explained on p. 88, when vapours are admitted into the evacuated space of the sorption tube, they are bound to expand and cool temporarily. The rates determined in the first few minutes may not therefore be very reliable. Secondly, though great care was taken to con-:trol the temperature of the thermostatic bath, variation of $\pm 0.75^{\circ}C$, could not be avoided in the simple type of bath used. This variation of temperature might cause slight condensation and evaporation on the surface of the fibre, and a slight error in the actual rate is also possible on this account. It would per-:haps be best to hold the sorption tube and the adsorbent well above the temperature of the liquid. But this would have meant rather too elaborate a thermostatic-apparatus. The conclusions drawn have therefore to be treated with some reserve. Neverthe-:less the work has shown that hydroxy compounds, including water and the aliphatic alcohols on the one hand and phenolic or

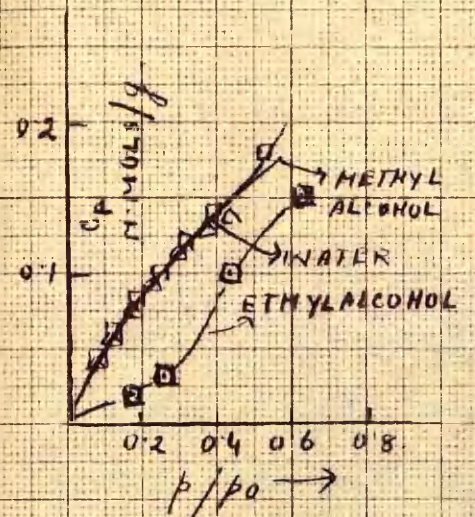


FIG. 67

SORPTION ISOTHERMS FOR WATER, METHYL ALCOHOL AND ETHYL ALCOHOL ON DRAWN NYLON AT 26 °C.

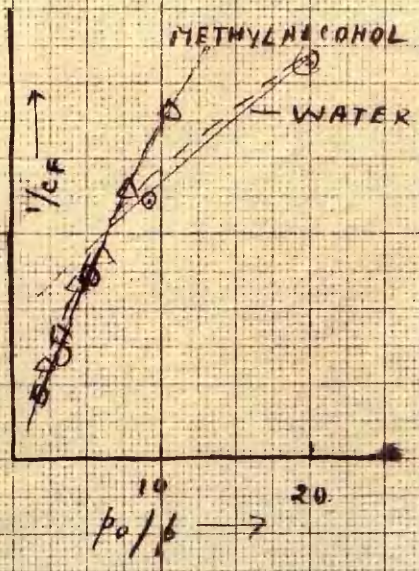


FIG. 68.

LANGMUIR CURVES FOR DATA OF FIG. 67.

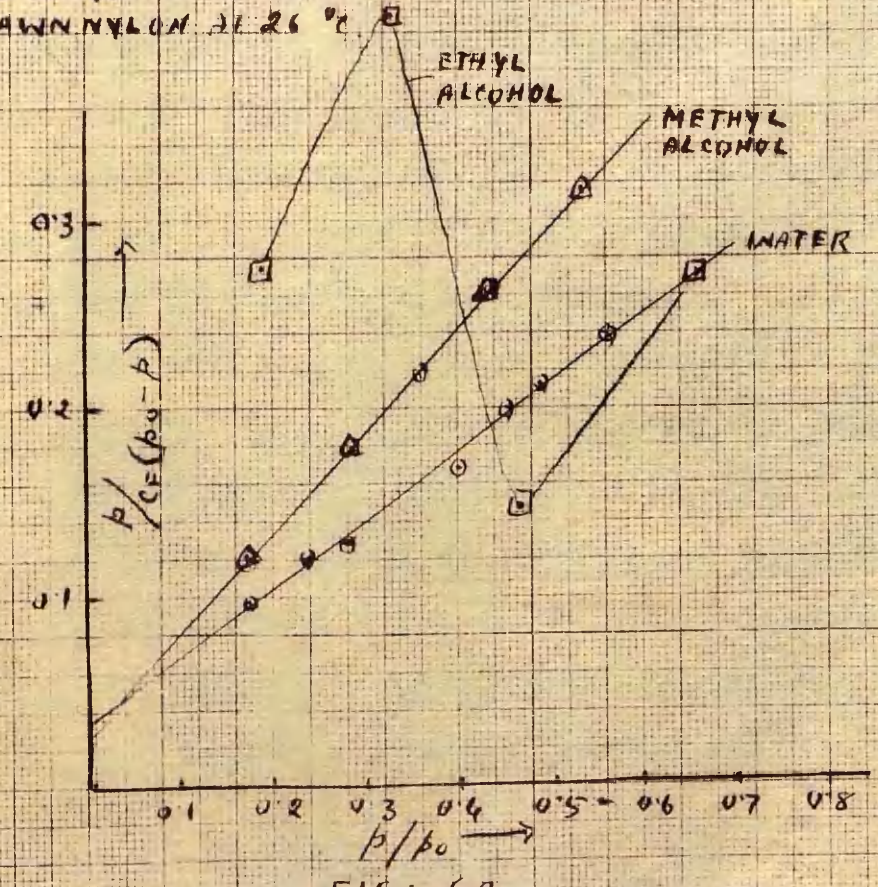


FIG: 69

BRUNAUR CURVES FOR THE ISOTHERMS OF WATER, METHYL ALCOHOL AND ETHYL ALCOHOL ON DRAWN NYLON.

Rate Studies from vapour phase

carboxylic or hydroxy compound like β-naphthol, alizarine or benzoic acid on the other, have an intrinsic affinity towards the fibres studied.

Secondly, it seems likely that the action of the hydroxy group in all these compounds (alcoholic, acidic or phenolic) mainly consists in hydrogen bonding with the amido hydrogen or the carbonyl oxygen of the -NH-CO- group.

Thirdly, the absence of any tendency towards equilibrium in most cases, and the increase in sorption rates observed after successive sorption and desorption cycles have very clearly proved that where combination with hydroxy groups is concerned, the surface of the fibres cannot be regarded as a rigid, 'free' and uniform one. If by some means (such as vaporisation at a high temperature) the adsorbate molecules can be made active enough, it may be possible to carry adsorption to almost an unlimited extent.

This conclusion has an indirect bearing on the behaviour of a number of dyes towards nylon and wool and probably any other fibre. The substantivity of a dye containing functional hydroxy groups and other groups may not just be restricted to the acidic or basic substituents in its molecule. It seems quite likely that the binding of the dye molecule to the fibre might be due at least as much to the 'hydrogen-bonding' substituents in its

molecule as to the main acidic or basic substituents.

Fourthly, the results of the rate experiments with dry va-:pours of hydrochloric acid, benzoic acid and acetic acid strongly suggest that weak carboxylic acids are adsorbed in the form of un-:dissociated molecules and not as their ions. The non-constancy in the limiting value of desorption observed in acetic acid on wool also supports the above conclusion and further shows that the acid does not preferentially attach itself to the more basic amino groups only; for if it did, the limiting value reached would cor-:respond to the number of free amino groups in the fibre.

In spite of the above important conclusions, the thermodyana-:mic treatment of the study leaves much to be desired. Though ac-:tivation energies at the zero point have been calculated for phenol, acetic acid and β-naphthol, and though their order is com-:parable (5,000 to 7,500 cal./g.mol.) it is realised that the re-:sults are to be regarded with some reserve. Also, the treatment of the kinetics of the sorption processes has not been complete. Apart from the experimental difficulties mentioned on p.88, the non-rigidity of the fibre surface would make any theoretical treat-:ment extremely difficult.

II

RESULTS AND DISCUSSION

D : Isotherm Studies from vapour phase.

II RESULTS AND DISCUSSION (continued)

D : Isotherm studies from vapour phase

(i) Isotherms for vapours of water, methyl alcohol and ethyl alcohol on drawn nylon

The results presented in this section were obtained in the initial stages of building up the apparatus. No air thermostat was used to surround the whole sorption apparatus, as was later done. As a result, the liquid bulb remained at the room tempera-:ture, 18-20°C. The sorption tube, however, was immersed in a water thermostat. The temperature of sorption in all cases was 25°C. The details of the experimental procedure are given in Appendix 2. It is to be noted here that since there was a dif-:ference of about 5 to 7°C. between the temperature of the liquid bulb and that of the sorption tube, the maximum relative pressures attained did not exceed about 0.6. By relative pressure is meant the ratio of the actual vapour pressure inside the sorption tube divided by the saturation pressure at the temperature of the ex-:periment.

The various theories of sorption are separately dealt with in Appendix 1. In this section, they will be applied to our experi-:mental data and an interpretation of the results will be given.

Tables 69 to 71 give the data for the three isotherms and Fig. 66 shows the isotherms for water, methyl alcohol and ethyl alcohol on drawn nylon. The percentage by weight of equilibrium sorption

is plotted against the relative vapour pressure. From the curves in Fig. 66, it might appear that the quantity of methyl alcohol taken by 1 g. of nylon is more than that of water at equal relat-:ive pressures. But this is only apparent, for, when the sorp-:tion is expressed as millimoles of sorbate taken by 1 g. of fibre the curves of methyl alcohol and water coincide. This is shown in Fig. 67. The same is not true for ethyl alcohol.

The fact that methyl alcohol and water show identical behav-:iour is very significant. Obviously the manner of sorption in both these cases must be identical.

An attempt was made to apply the Freundlich equation as well as the Langmuir equation to the data of Fig. 66. It was found, however, that these equations do not describe the isotherms satis-:factorily. The curves for the Freundlich equation are not shown here. An analysis of the Langmuir curves is given below.

The detailed derivation of the equation is given in Appendix 1 and the implications of the various assumptions are fully dis-:cussed there. According to Langmuir, the isotherm is given by

$$C_F = \frac{C_m \ b.p.}{1 + b.p.} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where

C_F = mols. of sorbate held by one g. of the fibre,

C_m = mols. of sorbate held by 1 g. fibre when the surface is fully covered by a unimolecular layer.

p = pressure of the gas in mm.

and b = a constant.

The equation can be rewritten as,

$$\frac{1}{C_F} = \frac{1}{C_m b} \cdot \frac{1}{p} + \frac{1}{C_m} \quad \ldots\ldots\ldots\

equation fitting a particular set of data can only be ascertained if the values of the constants in the equation are reasonable.

As pointed out above, the intercept of the Langmuir lines gives the value of $1/C_m$. This value for methyl alcohol and water can be read from the Fig. 68. It will be noted that at high values of sorption, the value of the intercept for both the vapours is the same, viz., 0.15 . Hence $C_m = {}^{1}/_{0.15}$ or 6.66.

Is this value of C_m for water and methyl alcohol reasonable? The following reasoning should make this point clear.

C_m actually represents the surface area covered by a uni-:molecular layer of the adsorbate. Now, if we assume that the molecules of water and methyl alcohol are spherical and that the area of packing would be given by the densest possible packing of these spheres, the larger the size of the molecules, the smaller should be the number of molecules required to make a unimolecular layer. Thus, for the larger methyl alcohol molecule we should expect a smaller value of C_m . But the values of C_m calculated by us are identical.

We therefore conclude that the Langmuir fit is fictitious and misleading. One would hardly expect a strictly unimolecular layer of adsorption for water and methyl alcohol on the surface of the nylon fibre.

Isotherm studies from vapour phase

Consider now the constant b in the Langmuir equation. Its explicit meaning is given by

$$b = \frac{\alpha_o \cdot e^{q/kT}}{k_o \cdot (2\ m.k.T)^{\frac{1}{2}}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where

α_o = condensation coefficient - a constant

q = heat of sorption

k = Boltzman Constant

k_o = a constant, and

T = the absolute temperature.

b could only be regarded a constant if q in the above equation is a constant. From the slopes of the two straight lines, the values of $C_m b$ can be calculated. And knowing C_m, the value of b could be calculated. This has been done, and the value of b for the two vapours is 3.7 . The value is equal for both the vapours, since the slopes are equal (See fig. 63) .

From equation 3, the value of q, the heat of sorption, could now be calculated. Normally one would expect higher values for the heat of sorption in the case of methyl alcohol. Without going into detailed calculation, it would be apparent that our values for both the vapours would be identical, since 'b' for both is the same.

Isotherm studies from vapour phase

It will thus be seen that though one would at first sight be tempted to say that the Langmuir equation is obeyed for the isotherms of water and methyl alcohol on drawn nylon, in actual fact it is not so. It is quite possible to draw smooth curves passing through all the points for water as well as methyl alcohol (see dotted lines in Fig. 68) and we therefore conclude that the Langmuir equation is not satisfactory to describe the isotherms of water and methyl alcohol on nylon.

What does this mean in the physical sense? Obviously the Langmuir equation will not be obeyed if either b or C_m is not constant. For b to remain a constant, q, the heat of sorption, must remain a constant; and for C_m to remain a constant, the number of sorption sites must remain a constant. In one case it would mean that the heat of sorption for the entire surface of nylon should be uniform and constant throughout the course of sorption. This could only happen if (i) all sorption centres are identical and if (ii) a strictly unimolecular layer is formed. As for (i), one could be fairly certain that the surface of nylon has identical sorption centres (the -NH-CO groups are here assumed to be the water attracting groups). As for (ii) however, we can only speculate. It is very unlikely that water or methyl alcohol would form a unimolecular layer on the surface of nylon.

Secondly, can C_m remain a constant? It would do so, if there was no breaking up of the fibre-structure such as by swelling. It is generally known that there is a definite though very slight swelling in water. But we do not know if methyl alcohol would cause swelling. Probably it does.

On the whole, therefore, the Langmuir equation has not helped us greatly to understand the sorption reaction between water or methyl alcohol on nylon.

Application of the B.E.T. Formula

The formula for multi-molecular adsorption (B.E.T. = Brunauer, Emmet & Taylor) is derived in Appendix 1. It is given by

$$\frac{p}{C_F (p_o - p)} = \frac{1}{C_m C} + \frac{C-1}{C_m C} \times \frac{p}{p_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where p = pressure of the vapour,

C_F = m.mol. of sorbate held by the fibre at equilibrium,

C_m = m.mol. of sorbate held by the fibre when a unimolecular layer covers the surface of the fibre,

And C = a constant given by

$$C = (a_1 g/b_1)\, e^{E_1 - E_L/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where $a_1 g/b_1$ = constant (very nearly equal to 1)

E_1 = heat of adsorption in the first layer,

E_L = heat of condensation of the liquid,

R = gas constant, and

T = absolute temperature.

A plot of the function $p/C_F (p_o - p)$ against p/p_o should give a straight line if the mechanism of adsorption was as postulated by the theory of multi-molecular adsorption.

In Fig. 69 are shown curves where the values have been so plotted. The constants C_m and C are calculated from the intercept and the slope. The value of $E_1 - E_L$ has then been calculated from the values of C, by substituting in equation 5. The following table gives a summary of the constants so evaluated. The last column gives the value of E_1 the heat of adsorption for the particular vapour.

Calculation of heats of adsorption and Brunauer constants for water and methyl alcohol on nylon.

TABLE 71A

	Intercept	Slope	Cm	C	E_1-E_L	E_1
Water	0.04	0.368	3.05	8.2	1250	10,600
Methyl alcohol	0.03		1.87	17.8	1715	10,100

It will be noted that the value of E_1 in the last column in the above Table is calculated by substituting the known values of E_L, the heat of vapourisation of the two liquids (9,350 cal./g.mol.

for water and 8,450 cals./g.mol. for methyl alcohol) (68C).

We applied the Langmuir equation to the data of our isotherms for water and methyl alcohol and came to the conclusion that the agreement of our data with the Langmuir concept was only apparent and not real. But should we consider the agreement with Brunauer's multimolecular concept real? The answer is in the affirmative. A glance at the above Table will bring out two important points.

Firstly, the calculated heats of adsorption in the first lay-:er are quite reasonable. The heats are nearly equal and their value is round about 10,000 calories per g.mol. Comparing this value with the heat of vaporisation (about 9,000 calories in both cases) its order is understandable. Further, since the heat of vaporisation of the two liquids is comparable with their heats of adsorption, the fundamental assumption of Brunauer, that the forces of attraction are similar to those operating in conden-:sation, is confirmed.

Secondly, whatever the mode of attachment, the surface cover-:ed by a unimolecular layer should be in inverse proportion to the molecular size. Of course, as on p.126, we assume that the mole-:cules are spherical and the surface covered represents the closest packing of the spheres. The ratio of the molecular size for water and methyl alcohol should be the same as the ratio of their

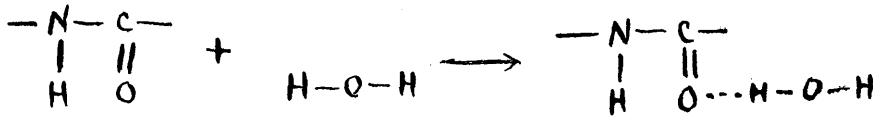
molecular weights, i.e. 18 : 32. The values of the two surface constants, it will be noted, are in the ratio of 3.05 : 1.87.

We therefore conclude that the isotherms for water and methyl alcohol obey Brunauer's isotherm equation quite satisfactorily.

Can anything be determined about the nature of the force of binding between the molecules of water and methyl alcohol on the one hand and the nylon fibre on the other? Do these molecules just condense on the surface of the fibre mechanically, or are there any specific forces of attraction between certain specific chemical groups in the fibre which bind the hydroxy groups in some special manner?

We recall here, our experiments on the rates of desorption of water and methyl alcohol on nylon (p.82; Fig. 41). We found that water was completely desorbed quite easily. But methyl al-:cohol could not be completely desorbed. If the molecules are held purely by surface forces of a physical character, methyl al-:cohol, which has a lower heat of vaporisation, should actually have been easier to desorb. It would therefore be reasonable to assume that there are specific groups towards which the hydroxy groups in these vapours are attracted and held. It is quite possible that the molecules are held by hydrogen bonding between the -NH-CO- groups and the hydroxy group, somewhat as follows:-

Isotherm studies from vapour phase



In Fig. 72 is also shown the curve constructed by applying Brunauer's equation to the isotherm for ethyl alcohol on drawn nylon. But as stated earlier, the sorption rate was actually too slow and it is believed that the values for the sorptions did not really represent equilibrium values. No significance can therefore be attached to the Brunauer curve in this case. It is for this reason also that we did not try to explain why the curve for ethyl alcohol did not coincide with those of water and methyl alcohol.

II D. Isotherm studies from vapour phase (Contd.)

(ii) Studies of water isotherms on wool-treated variously

Rate studies with acetic acid and hydrogen chloride vapours on wool revealed that the mode of combination of the acetic acid molecule with wool is essentially different than that of hydrochloric acid. Rate studies with acetic acid on wool, previously treated with sulphuric acid or with a dye solution, revealed that whereas in the former case the rate of sorption increased appreciably, in the latter it showed a considerable reduction. We therefore came to the conclusion that treatment with sulphuric acid exposes a larger number of sorption sites, and dyeing causes a reduction in the same. It was therefore decided to see if sorption isotherms for the smaller water molecules might throw some light on this problem.

Four types of wool were taken for the isotherm study.

1. Untreated wool. This was the same as that used for the rate of sorption of acetic acid, phenol, β-naphthol, etc.
2. Acid treated wool. The same as that used for acetic acid rate study, (p. 116.)
3. Dyed wool. The same as that used for acetic acid rate study. Dyed with Solway Blue B. as described on p. 116.

Isotherm studies from vapour phase

4. De-animated wool. This was prepared by treating one gram. of wool with 100 c.c. of an aqueous solution containing 21 c.c. of glacial acetic acid and 27 gms. of sodium ni-:trite (Van Slyke's reagent). The fibre was allowed to remain in contact with this solution for 48 hours at room temperature, squeezed, rinsed in cold distilled water, and washed in running tap water for 24 hours. Finally the fibre was steeped in a large quantity of distilled water (2 litres) for 24 hours and squeezed, dried and condit-:ioned at room temperature for 48 hours

The reason for including de-aminated wool in this series of experiments was to see if removal of the free amino groups in wool caused any change in the fibre structure as far as water sorption was concerned.

It is to be noted that the liquid bulb and the manometer were both maintained at 26°C. by surrounding them with an air thermostat. The sorption tube carrying the spiral and the fibre was maintained at 34°C. The difference in temperatures between the sorbate

liquid and the sorbent material was purposely maintained. In the first instance, this made the conditions more nearly comparable with those under which rates of acetic acid vapour were studied on wool samples similarly treated. (p.116). Secondly, any condensa-:tion effects on the fibre were thus avoided. A point to decide in calculating the relative vapour pressure was whether the satur-:ation vapour pressure taken into account should be that at 26°C or at 34°C. Since the relative vapour pressure was that of the vapour surrounding the adsorbent, it is clear that the saturation pressure at 34°C. and not at 26°C. must be considered.

The degassing and drying of the fibre was done at 0.0001 mm. pressure and at 34°C. The time of degassing was about four hours. It is generally believed that such a process of cleaning an adsor-:bent surface is not sufficient. Various investigators working on adsorbents such as charcoal or silica gel suggest that these should be repeatedly washed with the vapour to be studied before the adsorbent is truly clean. But it was difficult to see how such a procedure could be followed for the wool fibre. Repeated sorption and desorption, as we saw in the case of vapours of phenol -naphthol and benzoic acid, etc., tends to increase the effective surface area of the fibre. What would then be measured would be adsorption on a specially prepared surface and not on the true

surface of the natural fibre. In any case as Bull (44) has pointed out, whatever the pre-treatment given to the fibre, it has to be regarded as only arbitrary. It was therefore decided to subject the fibre to the minimum pre treatment.

Fig. 70 shows two isotherms for water vapour on untreated wool. The data are given in Table 72. The curve marked "1st sorption" shows the isotherm on wool which had been degassed at 34°C in the normal way. The same sample was subjected to desorp-:tion and it was found that the desorption was complete in four hours. A second isotherm was then determined on the same sample. This is shown in Fig. 70, by the curve marked "2nd sorption". It is to be noted that the sorption values under identical con-:ditions are distinctly higher for the second sorption.

In Fig. 71 are shown two similar curves for the first and second sorptions in the case of acid treated wool. The data are given in Table 73. It is extremely interesting to note that the difference of sorption noticed in untreated wool disappears and the two isotherms merge into one another. This would suggest that the opening up of the fibre achieved by means of a single sorption and desorption of water vapour equals that achieved under a very drastic acid treatment at boiling temperature - a conclus-:ion which is rather surprising.

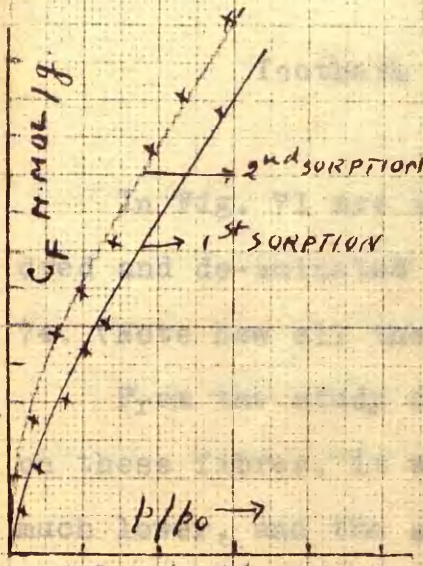


FIG. 70.

WATER ISOTHERMS FOR UNTREATED WOOL

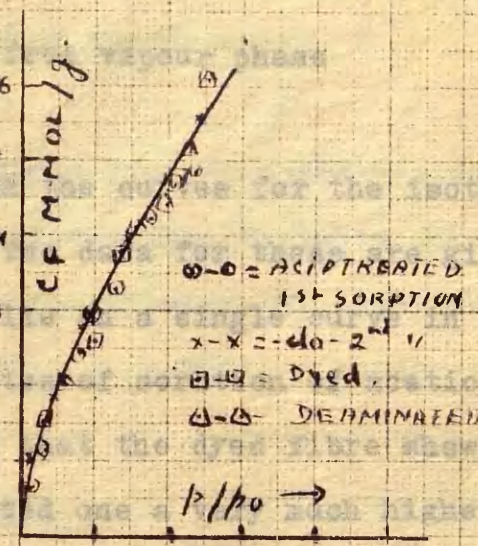


FIG. 71

WATER ISOTHERMS FOR ACID TREATED, DYED, AND DEAMINATED WOOL

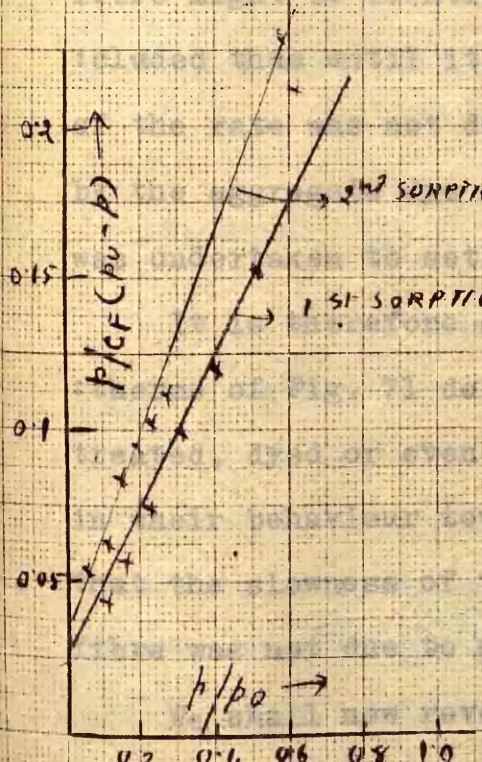


FIG. 72.

BRUNAUER CURVES FOR DATA OF FIG. 70.

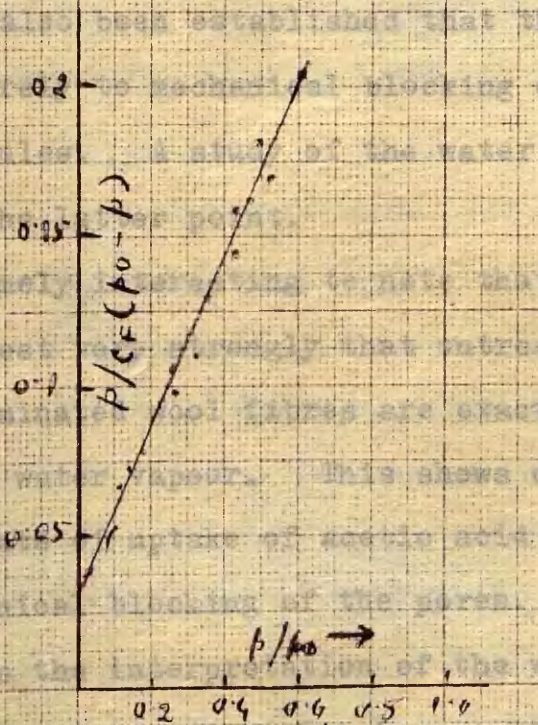


FIG. 73

BRUNAUER CURVES FOR DATA IN FIG. 71.

Isotherm studies from vapour phase

In Fig. 71 are also shown the curves for the isotherms on dyed and de-aminated wool. The data for these are given in Table 74. (Note how all the points lie on a single curve in Fig. 71).

From the study of the rates of sorbtion of acetic acid vapour on these fibres, it was noted that the dyed fibre showed a very much lower, and the acid treated one a very much higher, rate than the untreated one. This suggested that perhaps the points of attachment of the acetic acid molecule and the dye molecule on the fibre might be identical. But it could not be emphatically concluded thus until it had also been established that the slowness of the rate was not due merely to mechanical blocking of the pores by the aggregate dye molecules. A study of the water isotherms was undertaken to settle the latter point.

It is therefore extremely interesting to note that the isotherms of Fig. 71 do suggest very strongly that untreated, acid-treated, dyed or even de-aminated wool fibres are exactly similar in their behaviour towards water vapour. This shows definitely that the slowness of the rate of uptake of acetic acid on the dyed fibre was not due to mechanical blocking of the pores.

We shall now revert to the interpretation of the water isotherms themselves. Brunauer's equation has been applied to the isotherms in Figs. 70 and 71. The Brunauer lines so obtained are

shown in Figs. 72 and 73. The different constants in the equation have been calculated by the method followed for nylon (p.130). The heat of adsorption in the first layer, E_1, has been calculated from the value of the constant C. (p.129). These values are listed in the Table below:-

TABLE 75

Brunauer constants for water vapour on wool

		Cm.	C.	$E_1 - E_L$ Cal/g.mol.	E_1 Cal/g.mol.
Untreated wool (1st sorption)		2.82	8.8	1,330	10,360
" " (2nd sorption)		3.50	11.8	1,480	10,830
Acid treated, Dyed, and De-aminated	Wool	3.25	10.3	1,420	10,780

It is to be noted from the above Table that the values of C_m, the surface constant, are equal for acid treated wool, dyed wool and de-aminated wool. In other words, neither dyeing nor de-amination nor boiling in acid, causes any change in the total number of sorption sites for water. This again could only happen if the amino groups in wool had no part to play in the sorption of water vapour. Furthermore, a comparison of the value for the heat of adsorption for wool as calculated above, and for nylon as calculated on p.130, shows that these are identical for both of

these fibres. This fact and the above argument strengthens our belief that it is the -NH-CO- groups and not the $-NH_2$ groups in both the fibres which are responsible for water sorption.

We mention this because there still seems to be some controversy regarding the exact mode of attachment of water molecules to protein fibres. Cassie (69) believed that the carbonyl groups in keratin are the water attracting groups. Frey and Walter (70), on the other hand, studied the adsorption of water vapour on simple crystals of glycine, lencine and diketopiperizine, and came to the conclusion that water molecules are mainly attracted by the polar $-NH_3^+$ and $-COO^-$ groups. Our results seem to support Cassie's views rather than those of Frey and Walter.

Conclusions from the study of Isotherms in the vapour phase

Rate studies as well as isotherm studies of water and methyl alcohol vapours on nylon suggest that the mode of combination of these compounds on the fibre is similar. It is suggested that the mode of combination may be by hydrogen-bond formation at the -NH-CO- groups.

Isotherms for water vapour on wool lead to two interesting conclusions. Firstly, here also the -NH-CO- groups seem to be the water attracting groups. Our findings are thus more in agreement with Cassie's views (69) rather than those of Frey and Walter (70) who assume that water molecules combine with the polar side chains of the protein molecule. Secondly, the water isotherms on untreated, acid treated, dyed and deaminated wool show the remarkable fact that all these fibres give identical isotherms. The increase in the surface area or the number of amino groups has therefore no direct bearing on the course of sorption.

APPENDIX I.

Theoretical

Appendix 1 : Theoretical

In the foregoing discussion of our experimental results ref-:erence has been made to various theories on adsorption. These theories were taken for granted and their application to our own data was considered. We shall now discuss the theoretical as-:pect of the phenomenon of adsorption in detail.

The words 'absorption', 'adsorption', 'sorption','chemisorp-:tion' and 'activated sorption' have been used in the literature with specific meanings. When molecules of a gas or vapour are allowed to come in contact with an evacuated solid, some of them are held on the surface and some of them go into the interior. The former process is called adsorption, the latter absorption. The word 'sorption' is used to cover both of them. In these processes the sorbent as well as the sorbate retain their specific chemical nature. In some cases it might happen that a chemical reaction might occur between the sorbent and sorbate molecules. The phenomenon is then described as 'chemisorption'. In some others, very high energies of activation might be required before any sorption can take place. (See p. 49). The process is then known as 'activated sorption'.

Though the above classification is useful, it does not have any fundamental significance. Whatever term is used to describe

a particular process, the nature of binding between the sorbent and sorbate molecules is essentially the same in the thermodyan-:amic sense. Thus one may encounter very small heat changes in the process of sorption - one calls this physical adsorption. In ~~most~~ such cases, the forward process of sorption and the reverse process of desorption are comparatively easy. In most cases, desorption is more difficult than sorption (we found this true for the sorption of vapours of acetic acid, phenol and β-naphthol, etc. on nylon and wool); this is presumably due to high activation energies involved in the process. Finally, in some cases, sorp-:tion may be easy, and desorption may be very difficult or impos-:sible. The force of binding between the incoming molecule and the adsorbent molecule is so great that the chemical nature of the molecules is changed. This is chemisorption. It will thus be seen that, fundamentally, there is very little difference between what we call physical adsorption and chemisorption. The two broad types of sorptions may be separated by a variety of inter-:mediate stages. While considering the theoretical aspects of sorption, we shall ignore the actual nature of combination between the adsorbent and the adsorbate and treat all sorptions from the same thermodyanamic angle. To avoid confusion, we shall use the word 'adsorption' in its broadest sense.

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The theoretical aspect of adsorption may be considered under three convenient heads.

(A) The energetics of adsorption.

(B) The kinetics of adsorption.

(C) The adsorption equilibrium.■

■ The fundamental principles underlying kinetic considerations were developed in Section IIA, p.47. In this section we shall deal with the theoretical aspects of the energetics and the adsorption equilibrium.

Appendix 1 : Theoretical

A : The energetics of adsorption

(i) Energy and the two laws of thermodynamics

The fundamental assumption underlying all thermodynamic treat-:ment is that energy, like temperature, pressure, volume and so on, is a characteristic property of matter. We shall find it useful to analyse this fundamental concept of energy in detail.

One finds in the literature pertaining to thermodynamics, three important words sometimes very vaguely and confusingly used. These are: "energy", "work" and "heat". Of these, the words "energy" and "work" are complementary. Thus when work is done on a system, and provided there are no losses, energy is said to be stored by the system. Conversely, when there is an expenditure of energy by a system, work is said to be produced.

Energy and work may be of various kinds - mechanical, electri-:cal, chemical, thermal and so on. A body possesses mechanical energy due essentially to position or displacement of mass; elec-:trical energy due to the position or displacement of charged atoms and molecules within matter etc. When we come to thermal energy, we shall presently see that we enter a rather special field and the description of thermal energy needs a little clarification. By analogy one would be right to say that a body possesses thermal energy due to the position or displacement of 'heat'. It is here

that one sees how the word 'heat' may be used confusingly. When one speaks of mechanical energy, it is easy to differentiate be-:tween 'mass' and mechanical energy. Mass and mechanical energy are two different things. Hence if one ascribed thermal energy to the position or displacement of a quantity of heat, one would be forced to the conclusion that heat and thermal energy are two different things. Actually in many books and throughout most of the literature on thermodynamics, the term 'heat' is used both in the sense of thermal energy and in the sense described in the above definition of thermal energy. This makes it necessary at certain places to describe heat as a special form of energy. Thus Steiner (72) says the following about 'heat' and 'work'.

"In the first law equation we equate the increase in the intrinsic energy of a body with the sum of heat absorbed and work done on the body. A body may increase in energy by absorbing heat, work or both. In this sense, heat and work are equivalent to each other. There is a fundamental difference between the two, however, which is ignored by the first law. There are no limits to the transfer of work of the kind that restricts the transfer of heat. Work may be transferred from a colder body to a hotter body; it can be completely converted to heat. On the other hand heat does not pass spontaneously from a cold to a warm body."

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Actually, there is confusion not because "the first law" ig-:nores the difference between heat and work, but because one uses the word heat rather ambiguously. As we shall see later, both the first law and the second law do not ignore anything; their nature is different and both the laws are very precise and simple. Brönstead (73) makes this quite clear. We shall follow his method of approach for understanding the two thermodynamic laws.

All energy may be said to be composed of two factors. The intensive or the intensity factor and the extensive or the capa-:city factor. The intensity factor may also be termed the poten-:tial. Thus various forms of mechanical energy can be expressed as the products of force and distance, pressure and volume or mechanical potential and mass, while thermal energy can be expres-:sed as the product of temperature and entropy (see below). Chemical energy may similarly be split up into chemical potential and quantity of substance.

In its broadest sense, <u>the first law of thermodynamics,</u> is a law which enunciates the principle of conservation of energy. It attributes to every system a characteristic internal energy which can only be altered by interchange with the surroundings and which is uniquely determined by the state of the system. This internal

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energy may be possessed by a system in various forms which in themselves are interconvertible. When such an interconvertion of energy takes place within a system, the sum of the amounts of energy and work which have disappeared is zero.

In chemical thermodynamics, energy changes are accompanied not only by work but also by heat. The total sum of the energy changes is still zero. Thus if E was the increase in internal energy, Q, the heat absorbed and W the work obtained, then the first law of thermodynamics may be formulated as

$$E = Q - W \quad \ldots\ldots\ldots\

of the capacity factors of energy from one potential to another. The migration is always from a higher potential to lower one and never vice versa."

It is to be noted that the enunciation of the second law as above does not follow the conventional practice. We do not say, as is usually done, that the second law of thermodynamics states that though changes in energy and work might produce heat, heat cannot produce work or that heat does not flow from a colder to a warmer body. Though these are all statements of facts, they do not bring out the full significance of the second law. It is submitted that enunciation of the law as given above makes it more generally applicable to energy changes of all kinds and brings out the most important point that the law is concerned with the tendency towards equilibrium.

(ii) The concept of entropy and the second law

As stated before, thermal energy, like all other forms of energy, can be split up into two factors, the intensity factor called "temperature" in this case and the capacity factor. The name given to this capacity factor is "entropy".

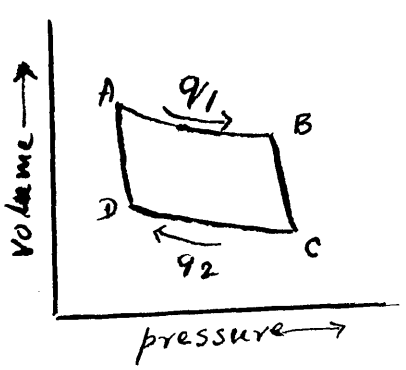
In this sense flow of thermal energy consists of the migration of the capacity factor entropy (S) from one temperature to another. As required by the second law, entropy can only be

transported from the higher to the lower temperature. Then if T_2 and T_1 are respectively the two temperatures, the work A done as a result of transport of the entropy S between T_2 and T_1 is given by

$$A = (T_2 - T_1) \quad S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

It will thus be seen that thermal energy like all other forms of energy can produce "work". The statement that "heat" cannot perform any "work" is thus misleading. The fact that thermal energy cannot flow from a lower temperature to a higher one is still true and it is this that is particularly stressed by the second law.

This concept of entropy is extremely useful to describe what are known as reversible and irreversible or spontaneous processes. A thermodynamically reversible process is one in which a system undergoing change is brought back to its original state without at the same time having caused any change in the surroundings. We shall illustrate this by making use of the famous Carnot's cycle.



The adjoining is a pressure-volume diagram representing one complete cycle of operations. A system at A is isothermally compressed and brought to

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B; $-q_1$ is the amount of heat evolved. It is then further compressed adiabetically along BC. It is again allowed to expand along CD isothermally and an amount of heat q_2 is absorbed. It is then brought back to A adiabatically.

Let the temperature along AB be T_1 and that along CD be T_2. Then since thermal energy can be expressed as the product of temperature and entropy, we have

$$S = \frac{-q_1}{T_1} = \frac{q_2}{T_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

For the complete reversible cycle,

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

If proper attention is paid to the sign of the heat change, i.e. whether the heat is absorbed or evolved, we find that, for this and for any other reversible process, in which the total quantity of energy does not change and the initial volume is restored,

$$\left(\sum dq/T\right)_{E,V,} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

In chemistry we do not deal with systems of constant energy content. Under these conditions the entropy does not remain constant for the equilibrium process.

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(iii) Entropy and adsorption

The concept of entropy has been used to investigate the isotherm for water vapour on wool by Cassie (69). We referred to his work in our introduction(P.12). Here we shall go into greater detail.

When, in any chemical reaction, the increase in the free energy (ΔG) is accompanied by increase in heat content or enthalpy (ΔH) and also an increase in entropy (ΔS) at a constant temperature T, the following relation holds

$$\Delta G = \Delta H - T\Delta S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The heat of wetting of keratin has been determined by Hedges (71), and Cassie derives an expression connecting the heat of wetting and the percentage absorption of water by assuming that there is no change in entropy, i.e. $T\Delta S = 0$. His reasoning is as follows:-

If entropy change is assumed to be zero, $\Delta G = \Delta H$ and the change in chemical potential ($\Delta\mu$) of water on adsorption is given by -

$$\Delta\mu = \frac{\partial(\Delta G)}{\partial n} = \frac{\partial(\Delta H)}{\partial n} = RT \log \frac{p}{p_0} \quad \ldots\ldots (7)$$

Where n = number of moles of water adsorbed by a fixed amount of keratin;

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T = absolute temperature;

R = gas constant per mole;

p = vapour pressure in equilibrium with sorbed water;

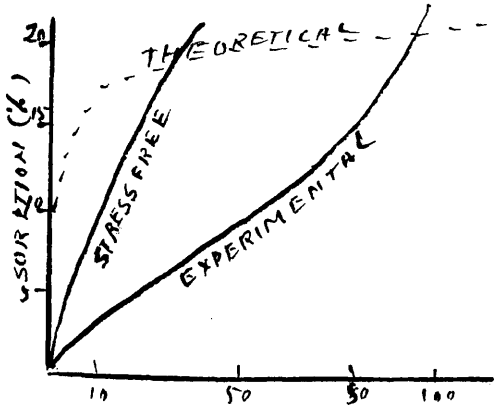
p_o = saturation vapour pressure of water at T^oC, and

$\frac{\partial(\Delta H)}{\partial n}$ = differential heat of wetting per mole and Hedges' data give in g.cal./mole, which

$= -3,320 + 126\ r + 0.054\ r^3$ .....(8)

Where r represents the percentage of water adsorbed by keratin.

The negative sign appears before the large constant term be-:cause heat is evolved when water is adsorbed by keratin. Equa-:tions 7 and 8 give the required relation between % adsorbed and relative humidity and a theoretical curve can be constructed. Cassie has done this. His curves are reproduced in the Fig. below. The broken curve is the theoretical curve obtained under the assumption that $\Delta S = 0$. The full curve is the experimental curve obtained by Hedges (loc.cit). The curves are not drawn to scale. The purpose here is only to show the difference in the shape of the cal-



REGAIN RELATIVE HUMIDITY CURVE FOR KERATIN

:culated and actual curve. In Cassie's own words,

"The difference between the broken curve ------ and the exper :imental curve shows how much of the shape of the isotherm is due to change of entropy of the keratin-water system during adsorp- :tion. Below 85% R.H. the observed adsorption is less than that predicted by the measured heat of wetting, and above this relat- :ive humidity the observed adsorption increases rapidly above the heat of wetting value. Below 85% R.H. the observed value of ΔG is smaller in magnitude than ΔH and since both are negative," equation 6, p.151, "shows that ΔS must be negative in this region. Similarly above 85 R.H. ΔS must be positive."

Two very important conclusions are drawn from the above.

The decrease in entropy at low regains is taken to show that the adsorbed water molecules have little or no freedom of move- :ment as compared to those in liquid water. In other words, the adsorbed water at low regains is held by definite chemical groups and hence is localised. Secondly, the increase in entropy after 85% R,H. is taken as a definite disproof of the capillary pore theory of adsorption which requires a definite reduction in the intrinsic energy or a decrease in the entropy.

(iv) <u>The heat of adsorption</u>

In the foregoing, we have reviewed in brief some basic thermodynamic principles. We are now in a position to discuss

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the significance of the heat-changes during adsorption.

If we admit 'n' moles of an ideal gas to a thoroughly evacuated adsorbent weighing 1 g, 'a' molecules of the gas will be adsorbed and a certain amount of heat will be liberated in the process. Let us assume that no external work is done during adsorption. If U_g is the energy of the gas per mole in the gas phase, and U_a the energy of the gas per mole in the adsorbed phase, the loss of heat from the system due to adsorption is,

$$q_i = n.Ug - (n-a).Ug - a.Ug = a\,(Ug - Ua) \quad \ldots\ldots\ldots\ldots(9)$$

The quantity of heat q_i is called the integral heat of adsorption. If we increase the amount of gas adsorbed by da, an additional amount of heat dq will be liberated. The differential coefficient $(\partial q_i/da)_T$ is called the differential heat of adsorption.

It should be noted that the integral heat of adsorption and the differential heat of adsorption may not always be the same. The differential heat will always be a truer measure of the heat of adsorption than the integral heat, because part of the heat of adsorption in the latter case might be utilised in doing some kind of work. Hückel (74) defines the integral (isothermal) heat of adsorption as

$$q \text{ isothermal} = q \text{ differential} + RT \quad \ldots\ldots\ldots\ldots\ldots\ldots(10)$$

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The isothermal heat may be directly measured calorimetrically. But it is not possible to measure the differential heat. This has always to be determined indirectly. The thermodynamic prin-:ciples involved in such calculations will now be discussed.

In an adsorbent-adsorbate system equilibrium is established when the isothermal transfer of an infinitesimal quantity of gas from the adsorbed phase to the gas phase brings about no change in the free energy of the system, i.e. when

$$\left[\frac{\partial F_g}{\partial n}\right]_T = \left[\frac{\partial F_a}{\partial a}\right]_T \quad \ldots\ldots\ldots\

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This equation can also be expressed in the form

$$H = F - T\left(\frac{\partial F}{\partial T}\right)_n \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

(See G. N. Lewis & M. Randall. Thermodynamics, New York, 1923, p. 162, equation 12).

Let now Hg and Ha represent the heat contents of the gas in the gas phase and in the adsorbed phase. Then the quantities Fg and Hg or Fa and Ha will be related as in equation 15 and 16 below

$$Hg = Fg - T\left(\frac{\partial Fg}{\partial T}\right)_n \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(15)$$

$$Ha = Fa - T\left(\frac{\partial Fa}{\partial T}\right)_a \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

Differentiating equation 15 with respect to n and equation 16, with respect to a, we obtain, equation 17 and 18.

$$\frac{\partial^2 Fg}{\partial n \partial T} = \frac{1}{T}\cdot\frac{\partial Fg}{\partial n} - \frac{1}{T}\cdot\frac{\partial Hg}{\partial n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(17)$$

$$\frac{\partial^2 Fa}{\partial a \partial T} = \frac{1}{T}\cdot\frac{\partial Fa}{\partial a} - \frac{1}{T}\cdot\frac{\partial Ha}{\partial a} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(18)$$

Subtracting 18 from 17, and considering the equality of $\frac{\partial Fg}{\partial n}$ and $\frac{\partial Fa}{\partial a}$ (see equation 11), we get

$$\frac{\partial^2 Fa}{\partial a \cdot \partial T} - \frac{\partial^2 Fg}{\partial n \partial T} = \frac{1}{T}\left(\frac{\partial Hg}{\partial n} - \frac{\partial Ha}{\partial a}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(19)$$

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We turn now to equation 9, where the terms Ug and Ua have been used for the energies of gas molecule in the gas phase and adsorbed phase respectively. Obviously,

$N.Ug = Hg$ and $N.Ua = Ha$ .....(20)

Substituting 20 into 19, and considering that for an ideal gas Ug is a function of the temperature only, i.e.

$$\frac{\partial Ug}{\partial n} = 0 \qquad \text{.....(21)}$$

We obtain,

$$\frac{\partial^2 Fa}{\partial a \partial T} - \frac{\partial^2 Fg}{\partial n \partial T} = \frac{1}{T}\left(Ug - Ua - a\frac{\partial Ua}{\partial a}\right) \qquad \text{.....(22)}$$

We further note that the right hand side in equation 22 is equal to q_d/T, for differentiating equation 9, we obtain,

$$\partial q_i = q_d = Ug - Ua + a\left[\frac{(Ug-Ua)}{\partial a}\right] \qquad \text{.....(23)}$$

And since

$$\frac{\partial Ug}{\partial n} = 0 \text{ (from equation 21)},$$

We can re-write equation 22 as

$$\frac{\partial^2 Fa}{\partial a \partial T} - \frac{\partial^2 Fg}{\partial n \partial T} = \frac{q_d}{T} \qquad \text{.....(24)}$$

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Let us now turn to the original equilibrium equation 11. Since Fg is a function of n and T and since Fa a function of a and T, the complete differential equation for the equilibrium is

$$\left(\frac{\partial^2 Fg}{\partial n^2}\right)_T \times dn + \frac{\partial^2 Fg}{\partial n \partial T} \cdot dT = \left(\frac{\partial^2 Fa}{\partial a^2}\right)_T \cdot da + \frac{\partial^2 Fa}{\partial a \partial T} \cdot dT \quad \ldots\ldots\ldots(25)$$

If we keep a constant, the term on the right hand side becomes equal to zero, and transporting terms we get,

$$\left(\frac{\partial n}{\partial T}\right)_a = \left(\frac{\partial^2 Fa}{\partial a \partial T} - \frac{\partial^2 Fg}{\partial n \partial T}\right) \Bigg/ \left(\frac{\partial^2 Fg}{\partial n^2}\right)_T \quad \ldots\ldots\ldots\ldots\ldots\ldots(26)$$

The free energy of a perfect gas can be expressed by the follow-:ing equation (~~84~~ 74 a).

$$Fg = n\, C_v\, (T - T.\ln T) + R.T.n.\ln n + (H_o - T\, S_o)n \quad \ldots\ldots(27)$$

Where

C_v = specific heat of the gas per mole at constant volume,

Hg = a constant heat content term and

S_o = a constant entropy term.

Partial differentiation with respect to n gives,

$$\left(\frac{\partial Fg}{\partial n}\right)_T = C_v\, (T - T.\ln T) + R\, T\, (1 + \ln n) + (H_o - T\, S_o) \ldots(28)$$

and differentiating again we obtain,

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$$\left(\frac{\partial^2 F_g}{\partial n^2}\right)_T = \frac{RT}{n} \qquad \ldots\ldots\ldots\

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$$\frac{R.\ T_1.\ T_2}{T_1 - T_2} \cdot \ln \frac{p_1}{p_2} = q \text{ isothermal} \quad \ldots\ldots\ldots\ldots\ldots\ldots (35)$$

Equation 35 can also be put in the form

$$\left(\frac{\partial \ln p}{(1/T)}\right)_a = - \frac{q \text{ isothermal}}{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (36)$$

For a small range of temperature $^{q}/_{R}$ can be assumed to remain constant and a plot of ln p against 1/T for a constant amount of gas adsorbed should then be a straight line, the slope of which gives the isothermal heat of adsorption.

(N.B. It is to be noted that in our heat calculations for the adsorption of aqueous phenol on nylon pp.24-26, we have used an equation similar to (35) and (36). We had assumed that phenol molecules in solution behaved as an ideal gas. Moreover, if equation 36 was to be obeyed, q/R must be a constant. We have implicitly assumed this also to remain constant within the temperature ranges of 25 to 40°C or 40 to 60°C. We have, however, no direct proof that the molecules of phenol in aqueous solution do necessarily behave as those of an ideal gas. Nor have we any proof to assume that q/R does remain a constant. It is on this account that the results of our heat calculations have been taken with some reserve.

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The same criticism can, however, be applied to the usual practice of determining the heat of reaction for all real gases or vapours from the data of their isotherms on an adsorbent at differ :ent temperatures. Such calculations have, however, been report- :ed in the literature from time to time for the adsorption of water vapour or the vapours of some organic compounds.)

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B : Adsorption Kinetics.

When two compounds interact to produce any physico chemical change, the extent of this change in unit time depends, in the ultimate analysis, on two important factors, viz.

(i) on the rate at which the molecules can come in contact with each other, and

(ii) on the existence of some sort of a physico-chemical potential difference between the two contacting species. If there was no such potential difference, according to the second law of Thermodynamics no such chemical change could take place.

Further, the rate at which molecules can come in contact would depend on the molecular velocities of the species. These velocities would in themselves be dependent on temperature, the higher the temperature, the greater the molecular velocities, and hence the greater the speed of the physico chemical change. If the two interacting species were a solid and a gas or a vapour, the influence of temperature on the gas would be far more effective in determining the rate than that on the solid. The chance of the gas molecules coming in contact with the molecules in the solid would also be increased if the number of molecules

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of gas in unit space surrounding the solid increased. It is be-:cause of this fact that pressure of the gas is important.

With respect to point (ii) mentioned above, it is clear that when a physico chemical change takes place, the equalisation of potentials must result in a change in energy of the reacting species. The amount of this energy change is also a very import-:ant factor in deciding the rate.

Let us imagine a hypothetical reaction between a molecule A and B such as

$$A + B \rightleftharpoons AB$$

According to the first law of thermodynamics, the stable configurations of A, B, and AB will all have characteristic ener-:gies of their own.

Let E_A, E_B and E_{AB} represent the energies of A, B and AB respectively.

Also let K_1 = velocity constant for the forward reaction,

K_2 = velocity constant for the backward reaction,

and K = equilibrium constant, defined as K_1/K_2.

Then if no work is done by or on the system, according to Vanthoff's equation (75) $\text{Ln } K = C - \frac{\Delta E}{RT}$ .....(1)

Where C is a constant and ΔE is the change in the internal energy

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of the system. If we express C as Ln C', we have from equation (1)

$$K = C' e^{-E/RT} \quad \ldots\ldots\ldots\

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Since $K = \frac{K_1}{K_2}$, or $\ln K, = \ln K_1 - \ln K_2$

$$\frac{d \ln K_1}{dT} = \frac{A_1}{RT^2} + B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

and, $$\frac{d \log K_2}{dT} = \frac{A_2}{RT^2} + B \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Where $A_1 - A_2 = \Delta E$ $\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$

It does not follow from this that B is independent of temp-:erature, but Arrhenius found emperically that the variation of the velocity constant k with respect to temperature can be expressed by the simplified equation

$$\frac{d \log K_1}{dT} = \frac{A}{RT^2}$$

$$\text{or} \quad \ln K_1 = C - \frac{A}{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

$$\text{or} \quad K_1 = C' e^{-A/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

Equation (9) clearly shows the effect of temperature as well as the activation energy A on the rate of reaction. The greater the value of A, the smaller the value of K. Similarly the high-:er the value of T, the greater is K. In other words the higher the energy of activation the slower the reaction. Also, for

constant values of A, i.e. for the same reaction, the higher the temperature, the greater the rate of a reaction.

Arrhenius interpreted the reaction by suggesting that there exists an equilibrium between 'normal' molecules and 'active' molecules, and that only the active molecules undergo chemical change. The active molecules are supposed to be formed from the normal molecules endothermically.

(iii) Langmuir's picture of the kinetics of adsorption

We are now in a position to understand Langmuir's concept of adsorption mechanism. According to him, when the molecules of a gas or vapour collide with the surface of a solid, the collision may be either elastic or inelastic. In some cases, very infre-:quently, the molecule may be elastically reflected from the sur-:face without any energy exchange taking place. Ordinarily, however, the collision is inelastic and the molecule stays in con-:tact with the surface for a certain amount of time. After a while, it leaves the surface and enters the gas phase. According to Langmuir (31) this time lag is responsible for the phenomenon of adsorption. According to this concept, the process of adsorp-:tion and desorption is continually taking place. The rate at which molecules collide against the surface determine the rate of adsorption and the rate at which they leave the surface determine

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the rate of desorption. When the rate at which molecules strike the surface is μ and the rate at which they leave the surface is γ the net rate of adsorption is,

$$\frac{ds}{dt} = \alpha\mu - \gamma \qquad \ldots\ldots\ldots\

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Where m is the mass of a molecule and K is Boltzman's constant; p and T are the pressure and temperature of the gas surrounding the adsorbent.

This should mean that the rate of adsorption should increase with increasing pressures and decrease with increasing mass of the molecule. Both these are generally true. In our own ex-:perimental results the rates of adsorption for water, methyl al-:cohol and ethyl alcohol decreased with increase in molecular size.

But Langmuir's concept is unable to give us the complete picture of the process of adsorption. As we saw earlier, the forward process of adsorption is also largely determined by the energy of activation, characteristic of the particular solid-gas system.

Similarly the rate of desorption would also be influenced by the activation energy. This point has been very clearly and simply explained by Taylor (66).

On this account one would expect the Langmuir concept to be inadequate. There are numerous experiments in the literature which in fact show the inadequacy of the Langmuir concept of ad-:sorption. The difficulties are particularly clearly seen in interpreting the rate data. We saw, in the case of our own

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experimental results, how very complicated was the interpretation of the rate data (Section II A, pp. 41-57)

There are other equally important considerations also. But these will be better discussed in the next section after de-:riving the Langmuir adsorption formula.

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C : The Adsorption Equilibrium

In the foregoing, we discussed some thermodynamic principles and the kinetics of adsorption. The study of adsorption at equilibrium is much more important. Its theory will be dis-:cussed in this section.

For a given gas and unit weight of a given adsorbent, the amount of gas adsorbed is a function of pressure and temperature only. When the pressure of the gas is varied and the tempera-:ture kept constant, the plot of the amount adsorbed against the pressure is called the adsorption isotherm. When the pressure is kept constant and the temperature varied one obtains the iso-:bar. A third method of expressing the results is by means of the adsorption isostere, i.e. the variation of the equilibrium pressure with respect to the temperature for a definite amount of gas adsorbed. The study of the isotherms is by far the most important. It allows one to evaluate the effect of pressure on the course of adsorption and also to calculate the isothermal heats. The isobars are not as frequently used as the isotherms, though the former help to determine the effect of temperature on adsorption and also to calculate the heats. If isotherms at varying temperatures are determined, one would be able to plot isobars as well as isosteres from the data.

Appendix 1 : Theoretical

A theory that gives a complete account of the adsorption iso-:therm accounts for the isobar as well as the isostere, since as stated above a series of isotherms can always be replotted in terms of isobars and isosteres.

It will be impossible to go into all the theories on adsorp-:tion found in the literature. The various theories can be broadly classified into two categories.

(i) Those which assume that the adsorption is essentially unimolecular in character (Langmuir (31), Williams (76), Henry(77) and Magnus (78). The approach to all these theories is essen-:tially the same, viz. that adopted by Langmuir and discussed by us on p.166.

(ii) Those on which the adsorption is assumed to be multi-:molecular. The multimolecular theories do not have a common approach like the unimolecular ones. In some, e.g. Polanyi (79) it is believed that the adsorption is due to long range attractive forces extending out from the surface of the adsorbent. In others,(80) the adsorption is supposed to be caused due to 'capillary condensation' inside the very small pores of the adsorbent. In yet another (38) the adsorption is assumed to follow Langmuir's mechanism.

Appendix 1 : Theoretical

As discussed on p./53, considerations of entropy change during adsorption indicate that the potential theory as well as the capillary condensation theory have to be discarded at least in their application to adsorption on textile fibres. We confine ourselves to the adsorption isotherms of Langmuir and Brunauer.

(i) Langmuir's adsorption isotherm

On p.166 we discussed Langmuir's visualisation of the adsorp-:tion mechanism and derived a very generalised form of his iso-:therm equation (equation 11, p.167). We may proceed now to de-:rive the explicit form of that equation. The quantities α, μ and γ represent the condensation coefficient, the rate at which molecules strike the surface and the rate at which they evaporate from the surface respectively. They are functions of p, T and S. 'S' denotes the surface concentration. Instead, we may use the fraction of the surface covered . Then, if S_1 is the sur-:face concentration when a complete unimolecular layer is formed,

$$\theta = S/S_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Langmuir introduced two assumptions in the derivation of his equa-:tion. The first is that the probability of desorption of a molecule from the surface is the same whether the neighbouring positions on the surface are occupied by other molecules or not.

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This is equivalent to assuming that the forces of interaction be-:tween the adsorbed molecules themselves are negligible. It is expressed by the equation

$$\gamma = \gamma_1 \theta \qquad \text{.....(14)}$$

Where γ_1 is the rate of desorption from a completely covered sur-:face. Equation (13) also implies a uniform heat of adsorption over the entire surface. In other words, all the adsorption sites on the surface must be identical.

Langmuir's second simplifying assumption is that every mole-:cule from the gas phase striking a molecule adsorbed on the sur-:face is elastically reflected and only those molecules condense that strike the bare surface. This is expressed by

$$\alpha \mu = \alpha_0 (1-\theta) \mu \qquad \text{.....(15)}$$

where α_0 is the condensation coefficient on the bare surface and $1 - \theta$ is the fraction of the surface that is bare. This assump-:tion is equivalent to the postulation of unimolecular adsorption. The value of α_0 is always close to unity because elastic collisions are negligible on the bare surface.

Substituting equations (14) and (15) into (11) and solving for θ, one obtains the Langmuir isotherm equation

$$\theta = \frac{\frac{\alpha_0}{\gamma_1} \cdot \mu}{1 + \frac{\alpha_0}{\gamma_1} \cdot \mu} \qquad \text{.....(16)}$$

Appendix 1 : Theoretical

One may write this equation in the form

$$\theta = \frac{b \cdot p}{1 + b \cdot p} \qquad \ldots\ldots\ldots\

Appendix 1 : Theoretical

Equation 21 is the generalised form of the Langmuir adsorption isotherm.

(ii) The adsorption isotherm of Brunauer, Emmette and Teller

Brunauer (Physical adsorption of gases and vapours, p.150) classifies the isotherms reported in literature into five main types. These are reproduced in Fig. 5, p.21-23.

Of these, type I isotherm represents unimolecular adsorption. The most successful interpretation of isotherm of this type has been given by Langmuir. The type II isotherm has been generally attributed to multimolecular adsorption. The potential theory and the capillary condensation theory both deal with multimole-:cular adsorption but neither accounts for the shape of the iso-:therm. Further, the five isotherm types represent closely re-:lated phenomena, and Brunauer's theory is the first attempt to give a unified theory of physical adsorption. Its most general equation (equation 31 below) includes all the five isotherm types as special cases and describes the shape of each isotherm type through the entire range of adsorption, from zero pressure to saturation pressure.

The fundamental assumption of the theory of multimolecular adsorption is that the same forces that are active in condensa-:tion are also producing the phenomenon of Van der Walls adsorp-

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:tion. On this assumption one can derive an isotherm equation that is a generalisation of Langmuir's treatment of unimolecular adsorption.

Let S_0, S_1, S_2, ... S_i ..... represent the surface area that is covered by 0, 1, 2, ... i, ... layers of adsorbed molecules. Since at equilibrium, S_0 must remain con-:stant, the rate of condensation on the bare surface must be equal to the rate of evaporation from the first layer, or

$$a_1.p.S_0 = b_1.S_1.e^{-E_1/RT} \quad \text{.....(22)}$$

Where p is the pressure, and E_1 is the heat of adsorption in the first layer, and a_1 and b_1 are appropriate constants. This is essentially Langmuir's equation for unimolecular adsorption.

At equilibrium S_1 must also remain constant. It follows therefore that

$$a_2\ p.S_1 = b_2.S_2.e^{-E_2/RT} \quad \text{.....(23)}$$

Or, the rate of condensation on the top layer is equal to the rate of evaporation from the second layer. In equation (22), E_2 is the heat of evaporation from the second layer and a_2 and b_2 are constants. Extending the same arguments to S_2, S_3 etc. we obtain,

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$$a_3\, p.S_2 = b_3\, S_3.e^{-E_3/RT} \quad \text{.....(24)}$$

$$\vdots \qquad\qquad \vdots$$

$$a_i\, p.S_{i-1} = b_i.S_i.e^{-Ei/RT}$$

The total surface of the adsorbent is given by

$$A = \sum_{i=0}^{i=\infty} S_i \quad \text{.....(25)}$$

and the total volume adsorbed is

$$V = V_0 \sum_{i=0}^{i=\infty} i S_i \quad \text{.....(26)}$$

Where V_0 is the volume adsorbed on one square centimeter of the adsorbent surface when it is covered with a complete unimolecular layer. It follows that

$$\frac{v}{a V_0} = \frac{V}{V_m} = \sum_{i=0}^{i=\infty} i S_i \Big/ \sum_{i=0}^{i=\infty} S_i \quad \text{.....(27)}$$

Where Vm is the volume adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer.

The summation indicated in equation (27) can be carried out if one makes the simplifying assumption that

$$E_2 = E_3 = \ldots = E_i = E_L \quad \text{.....(28)}$$

Where E_L is the heat of liquifaction and

Appendix 1 : Theoretical

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = \ldots\ldots \frac{b_i}{d_i} = g \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (29)$$

Where g is an appropriate constant. This is equivalent to assuming that the evaporation condensation properties of the molecules in the second layer and the higher adsorbed layer are the same as those of the liquid state. Brunauer regards these assumptions as reasonable, since "the adsorbate molecules in the first layer are in contact with the adsorbent, but in the second layer they are in contact with other adsorbate molecules only. Since the van der Waals forces have a very short range of action, the effect of the adsorbent is probably quite small already in the second layer. It is therefore probable that the structure of the second layer is quite similar to that of the liquid."

We shall not go into the detailed mathematical derivation of the various summation steps here. Suffice it to note here that Brunauer considers two specific cases:

(i) When the adsorption takes place on a free surface, at p_o, the saturation pressure of the gas, an infinite number of layers can build up on the adsorbent. In such a case the final solution of equation (27) is given by

$$\frac{p}{v\,(p_o - p)} = \frac{1}{VmC} + \frac{C - 1}{VmC} \cdot \frac{p}{p_o} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (30)$$

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Where p = pressure of gas, at the temperature of experiment,

p_o = saturation pressure at the same temperature,

C = a constant given by $e^{(E_1 - E_L)/RT}$

and V_m = volume of gas which is adsorbed in one unimolecular layer.

(ii) If the adsorption does not take place on a free surface but in a limited space, then at saturation not an infinite but a finite number of layers can build up on the surface of the adsorbent. Let us imagine, for example, that the adsorption occurs in a capillary consisting of two plane parallel walls. If the maximum number of layers that can be adsorbed on each wall of the capillary is N, then the summation of the two series in equation (27) is to be carried to n terms only and not to infinity. One obtains then,

$$\frac{v}{V_m} \quad \frac{Cx}{1 - x} \cdot \frac{1 - (n + 1)\, X^n + nx^{n+1}}{1 + (c - 1)\, X - CX^{n+1}} \qquad \ldots\ldots\ldots\ldots\ldots(31)$$

Where $x = p/p_o$ and v_m and C have the same meaning as before. It is not impossible that other factors than capillaries can limit the maximum number of layers that can be adsorbed. In such a case, equation (31) still remains valid.

Equation (31) has two important limiting cases. If $N = 1$, it reduces to

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$$\frac{V}{Vm} = \frac{\frac{C}{po} \cdot p}{1 + \frac{C}{po} \cdot p.} \quad \text{.....(32)}$$

A comparison of equation (32) with equation (17) p. 174 shows that this is Langmuir's equation with the constant b having the value c/po. The other limit is when n = ∞ i.e. when the adsorption takes place on a free surface. In this case equation (31) reduces to equation (30). It is also to be noted that when X is small and N is at least as large as 4 or 5, equation (30) becomes a very good approximation to equation (31).

Since in the derivation of equation (31) the forces of cap-:illary condensation were neglected, the equation is regarded by Brunauer as more or less a rough approximation in the higher pressure region. He has also derived a suitable equation which takes into consideration the forces of capillary condensation. Such an equation explains satisfactorily isotherms of types IV and V in Fig. 5, p.21 . But, in the field of adsorption on tex-:tile fibres such isotherms are seldom met. It is therefore not considered necessary to go into any detailed discussion of such an equation.

Equation (31) includes as special cases the isotherm types designated as I, II and III in Fig. 5. If N = 1, it reduces to

Appendix 1 : Theoretical

(32) and we obtain a type I isotherm. If $N > 1$, we obtain either type II or type III isotherms depending on the value of the constant C. If the attractive forces between adsorbent and the adsorbed gas are greater than the attractive forces between the molecules of the adsorbate in the liquid state, i.e. if $E_1 > E_L$ in equation (30) we obtain S shaped type II isotherms. If on the other hand the forces between adsorbent and adsorbate are small, i.e. if $E_1 < E_L$, we obtain type III isotherms.

Appendix 1 : Theoretical

D : Theories of adsorption and textile fibres

In the previous sections, a very general account of the fundamental theory of adsorption was given. An attempt will be made in this section to point out their limitations, especially when they are to be applied to adsorption in relation to textile fibres.

In Langmuir's derivation of the adsorption isotherm the following are the fundamental assumptions:-

(i) That the surface of the adsorbent behaves as a free and uniform surface. That is to say, it has sorption sites with a uniform heat of adsorption.

(ii) That the adsorption is unimolecular.

Both these assumptions are not valid when adsorption on textile fibres is considered. It seems to be quite definite that the surface of the textile fibres, especially that of wool, silk and other protein fibres, has sorption sites which are not uniform with respect to their heat of adsorption. There are a variety of functional groups such as the -OH, -COOH, $-NH_2$, -NH-CO- etc. and these are bound to have a specific influence on the incoming adsorbate molecules, and, depending on the nature of the functional group in the adsorbate, the heat of adsorption on these adsorption sites is bound to be different. Moreover, the

second assumption that the adsorption is unimolecular is too simple, and as Brunauer's treatment clearly shows, it is also incorrect.

For these reasons, a new approach had to be made, and Brunauer's multimolecular theory is without doubt a very significant advance in the general field of adsorption.

It seems, however, that even this theory is not without its shortcomings when it has to be applied to textile fibres. The fundamental assumptions of this theory are:-

(i) That the forces operating in adsorption are of the weak or van der Waal's type.

(ii) That adsorption could be both unimolecular and multimolecular in nature. When the adsorbed layer is more than one molecule thick the heat of adsorption in the first layer only is truly indicative of the heat of adsorption between the adsorbate and adsorbent. The molecules of the adsorbate in the first layers behave as those in the liquid state and the heat of adsorption in the second and subsequent layers is the same as that of liquefaction.

The second of these assumptions is rather difficult to visualise, for, if the molecules in the first adsorbed layer did behave as those in the liquid, since the vapour under study is

already in equilibrium with the liquid, it is very unlikely that a second adsorbed layer should form at all. But experience shows us that multilayers <u>are</u> formed. We must therefore conclude that the first adsorbed layer still contains molecules which are not strictly similar to those in the liquid.

Apart from these objections, both the Langmuir theory and the Brunauer theory suffer from one very important omission. Neither lays enough stress on the nature of the adsorbent surface. Both visualise a constant and uniform surface with identical sorption centres having uniform heat of adsorption. Textile fibres and most of the other high molecular weight polymers are not so simple in their structure as to allow the above assumption to be true. That these fibres swell on adsorption is well known. If, as is believed, adsorption causes displacement of the molecular chains, the surface can hardly be regarded as a constant and rigid one. No theory so far put forward takes into account this important point. Whenever adsorption is complicated by swelling, all such theories which are based on the assumption of constancy of the adsorbent surface are bound to fail.

A new approach therefore seems to be necessary. Hailwood and Horrobin seem to have felt likewise. They have put forward a rather simple mechanism to explain the adsorption of water

vapour by polymers. The adsorbed water is assumed to exist in two states; first, water in simple solution, and secondly, water conbined to form a hydrate with a definite unit of the fibre mole-:cule. It is then simply assumed that the three species present in the solid phase - dissolved water, unhydrated molecules, and hydrated molecules.- form an ideal solution. This ideality in the solid phase allows the adsorption isotherm and also the equa-:tion connecting volume and amount of adsorbed water to be expli-:citly derived and tested by comparison with experimental data. We shall not go into details here. It is enough to note that the isotherm derived from such a simple model fits rather surpris-:ingly the data of adsorption of water on various polymers. In fact the fit of their new isotherm with experimental data is so good that the authors "believe that the simple model on which it is based has considerable validity. The fit is certainly better than can be obtained by any previously published isotherm."

One, however, wonders if the authors' claim is really justi-:fied. They treat the fibre as a rigid, constant and uniform surface and this can be questioned. Furthermore, if the water were to form a monohydrate (as the authors assume) with a defi-:nite fraction of the polymer molecule, it is possible from their formula to calculate the molecular weight of the polar unit

combining with one molecule of water. The authors themselves have made such calculations, and it is found that these values are much lower than expected. They explain this by saying that the 'crystalline' part of the fibre surface is not accessible to the water molecules. As pointed out on p. 81, modern studies with the electron microscope cast a serious doubt on the existence of "crystalline" and "amorphous" regions in textile fibres or high polymers. Our own work, as we have discussed at various places, confirms this view. One therefore has to take Hailwood and Horrobin's suggestions with great caution.

It is felt that the structure of the textile fibre is rather too complex to allow of any simple and straightforward theoretical treatment of adsorption. If nothing else, the failure of numerous theories so far proposed to explain adsorption on textile fibres is enough to convince us that such is the case. It would perhaps be more useful to direct attention to modifying the experimental approach to the problem so that the complexity of the structure of the fibre is minimised. This could be done in two ways.

(i) By choosing adsorbates which do not swell or alter the structure of the fibre on the one hand, and are so small in molecular size that they have a very easy access to all the parts of

the fibre. Adsorption of gases like hydrogen, oxygen and nitro-:gen etc. might be quite helpful.

(ii) By subdividing the fibres mechanically without alter-:ing the chemical nature of the fibres. If the sub-division is fine enough, vapours of various compounds could be studied with respect to adsorption.

The first approach might help to elucidate the structure of the fibres; the second might help to give an insight into the mode of attachment of various compounds - simple organic vapours, intermediates and also perhaps dyes.

APPENDIX 2

Materials and Methods

APPENDIX 2

Materials and Methods

Adsorbents

Nylon and wool have been used as adsorbents in the present work. Both drawn and undrawn nylon have been studied. The drawn nylon was "15" filament yarn of 40 denier. The undrawn fibre had a diameter of 0.025" . Both of them were obtained from the same source, I.C.I. Ltd., (Plastics Division), and it is believed that chemically both were of equal purity. In some experiments, nylon powder was prepared by dissolving the drawn fibre in phenol and reprecipitating by dilution. The wool used was sheep wool from a Lincoln fleece. Root ends of fleece were specially picked and carded. The pretreatment of the adsorbent was uniform throughout the experiments. The procedure for each type of yarn is given below:-

Drawn and undrawn nylon

The fibres were of sufficient purity for only a light scouring treatment to be necessary. For this purpose 5 g. of nylon (drawn or undrawn) was scoured in one litre of distilled water containing 0.6 g. Teepol X (Shell Chemicals Ltd.) and 1 c.c. of 0.88 ammonia, at 60°C.for 20 minutes; it was then thoroughly washed in distilled water and dried in an air oven at 60°C.; finally it was conditioned at room temperature for 48 hours, cut into suitable sizes and bottled.

Materials and Methods

Powdered nylon

1 g. of scoured nylon was dissolved in 30 g. molten phenol at 60°C.; when solution was complete, it was poured into a glass beaker containing two litres of boiling distilled water, with constant stirring. The nylon separated as a fine precipitate. The precipitate was then filtered and washed as thoroughly as possible with distilled water. It was found that washing out of the last traces of phenol was very slow. Hence the powder was subjected to Soxhlet extraction with 95% alcohol until free from phenol. Sixteen hours extraction was found to remove all traces of phenol from the powder. It was then rinsed in distilled water again, and dried at 60°C. in the air oven and conditioned for 48 hours.

Wool

About 10 g. of specially picked root ends of fleece wool was given a very light ammonia scour in the cold. This helped to remove adhering dirt. It was washed in distilled water and dried at 60°C. in the air oven. The dry fibre was next subjected to ether extraction in a Soxhlet apparatus for 24 hrs., dried at room temperature, steeped in distilled water overnight, and squeezed and dried in the air oven at 60°C. It was then conditioned at room temperature for 48 hours and finally stored in a well corked bottle

Materials and Methods

Adsorbates

The adsorbates used and their specifications of purity, etc., are given below:-

Water

Distilled water obtained from a tinned copper still was re-:distilled from a Pyrex glass distillation flask.

Methyl alcohol

This was dehydrated by refluxing over lime for 12 hours and distilling off the alcohol. The distillate so obtained was further refluxed over magnesium moistened with methyl iodite. After twelve hours refluxing, the alcohol was carefully distilled into a receiver protected from atmospheric moisture.

Ethyl alcohol

The same procedure as for methyl alcohol was followed.

Phenol, Resorcinol, β-Naphthol and Benzoic Acid

"Analar" qualities of these compounds were used.

Benzenesulphonic acid

A 32% solution, obtained from British Drug Houses Ltd., was used. This is believed to be 100% pure.

Alizarine

Crude alizarine paste (I.C.I.) was dried and then directly sublimed over a Bunsen burner. About 1 g. was kept in a nickel

crucible, covered with a filter paper, the sublimate collected on the cooler parts of the filter paper as long orange red needles melting at 292°C.

Aniline: B.P. quality, redistilled.

Ethyl acetate, methyl malonic ester, acetone and pyridine B.P. quality.

Methods for the determination of the absorption rates and isotherms for aqueous phenol, resorcinol, benzoic acid, benzenesulphonic acid, and aniline.

The fibre (1 g.) was placed in a dry conical flask of a suitable capacity. In all cases the adsorbent-adsorbate ratio was kept constant. To vary the concentration, the material-liquor ratio was varied. The adsorbent-adsorbate ratios were as follows-

Nylon: Phenol	=	2:1
Nylon: Resorcinol	=	2:1.5
Nylon: Benzoic acid	=	20:1 ⊠
Nylon: Aniline	=	2:1
Nylon: Benzenesulphonic acid	=	1:1

⊠ The solubility of benzoic acid in water is very low (0.29 g. in 100 c.c.) and hence the adsorbent-adsorbate ratio in the bath had to be very high in this case.

The conical flask containing the fibre and the solution was placed in a water thermostat held at the desired temperature. When rates were to be measured, eight identical weights of fibre were allowed to react with identical volumes of adsorbate solution, in different conical flasks, and an aliquot amount of solution was pipetted out from each flask after successive intervals of time and titrated. When isotherms were to be determined, the eight conical flasks contained varying concentrations of the adsorbate. An aliquot quantity of solution was pipetted out after equilibrium was reached and estimated by titration.

Methods of estimation:

Phenol, resorcinol, and aniline

A 0.1 N bromine solution was prepared by dissolving 2.76 g. of potassium bromate (Analar) and 15 g. of potassium bromide (Analar) in water and diluting to 1000 c.c. The solution was standardised against 0.1 N sodium thiosulphate by adding potassium iodide and hydrochloric acid and titrating the liberated iodine in the usual manner.

The solution of phenol, resorcinol or aniline was adjusted to about 0.1 M strength; 15 c.c. of this solution was mixed with 50 c.c. of water, 500 c.c. in a glass-stoppered bottle, and 5 c.c. of concentrated hydrochloric acid added. The standard 0.1 N

bromine solution was added from a burette, with constant shaking, until a permanent yellow colour was obtained. The temperature during this addition was not allowed to exceed 20°C. to prevent loss of bromine. The bottle was stoppered and shaken for one minute, 0.5 c.c. of 20% potassium iodide solution added and the free iodine titrated against N/10 sodium thiosulphate using starch as indicator.

1 c.c. of N/10 bromine ≡ 0.001568 g. phenol

≡ 0.001835 g. resorcinol

≡ 0.001564 g. aniline

Benzoic acid and benzene sulphonic acid

These were estimated by titration with carefully standard-:ised solutions of 0.01 N caustic soda. A micro-burette was used for titration. In each case a blank reading for acid-free water was taken to correct for the presence of any dissolved carbon dioxide.

Determination of vapour-phase sorption

(i) Use of a glass spiral for weighing small quantities

The underlying idea of the whole technique is to use a sen-:sitive spiral McBain's spring balance (64) to weigh very min-:ute quantities. It is well known that the load--extension

relationship for a spiral of any material is very nearly linear within a certain range of load. The extensibility of the spring is governed by the following three factors:-

(i) The diameter of the spiral: the bigger the diameter, the larger the extension per unit load.

(ii) The diameter of the fibre used for the spiral: the smaller the diameter the greater the extension per unit load.

(iii) The number of turns per unit length: the greater the number of turns, the greater the extension.

Tables 8 and 9 give typical load-extension data for two Pyrex glass spirals, one having a fibre diameter of 0.008" and a coil diameter of 0.75"; the other has a fibre diameter of 0.009" and a coil diameter of 0.5". The number of turns per inch in both cases was 12, and the total length taken was 9 cm. in both cases. Figs. (31) and (31a) represent graphs drawn with loads as abscissae and extensions as ordinates. It will be noticed that the larger diameter of the coil in spiral No. 1 has increased the sensitivity of the spring.

McBain himself recommends the use of quartz spirals in pre-:ference to metals, alloys, or glass. The reasons for this are obvious. Apart from being useless for corrosive vapours, metals possess a very high coefficient of expansion under heat and during

accurate measurements differences in temperature might produce appreciable errors.

For glass and fused silica, the thermal coefficients of expansion are very low. This is one big advantage in favour of glass and fused silica.

Table 9a gives values for the thermal expansion coeffi-:cients of different metals and different varieties of glass. It will be noticed that whereas quartz has as low a value as 5.8×10^{-7}, most varieties of glasses and different metals have a very large thermal expansion coefficient. Fig. (30a) gives the effect of temperature on expansion (65) for various mater-:ials. It will be noticed that fused silica has almost negli-:gible expansion within as wide a temperature range as 0° to 600°C. It has also a perfect linear relationship. Pyrex glass is next best in the series. However, above 300°C., it does not behave linearly. Most of the metals have a very high thermal expansion though they show linearity.

Though the use of fused silica for spirals is best, making silica spirals is rather a difficult task. Glass springs, however, are more easily made. Moreover, as Fig. (30a) shows, Pyrex glass possesses a tolerably low thermal expansion coeffi-:cient and behaves linearly with temperature below 300°C.

Materials and Methods

Since none of the textile fibres could be studied above 100°C., it was thought worth while to use glass springs.

It was noticed during the course of a few experiments that glass showed a tendency to suffer a permanent extension when heated under load for a long time. The trouble was easily re-:medied by heating the spiral with maximum load at a temperature of about 200°C. for four hours. After this annealing treatment, repeated heating of the loaded spiral at temperatures below 100°C did not produce any permanent extension. The Table below gives figures to illustrate this.

TABLE 96

Effect of heating on a glass spiral under load

Original length 25°C.	16.209 cm.
Spring heated at 200°C. for 6 hours, cooled to 25°C., length read at 25°C.	16.239 cm.
Spring heated again at 100°C. for 3 hours, cooled to 25°C., length read at 25°C.	16.236 cm.

Materials and Methods

Measurement of the length of the spiral

The length of the spiral was read by means of a cathetometer rigidly mounted on a stand. It was always important to ensure that the top and bottom ends of the hooks were in the same vertical plane so that the focussing could be done at or near the cross wires in the eyepiece of the cathetometer. The floor of the room in which the experiments were carried out was made of wood and the readings tended to vary due to vibration of the floor. Both the top and bottom end were therefore read for each set of readings so that the length of the spiral was always obtained by difference.

The limit of accuracy attainable is quite good. Spiral No. 1, for example, gave an extension of 12.69 cm. per g. of load. Since the cathetometer used for measuring the length of the spiral could read to 0.001 cm. it is seen that an extension of 0.002 cm. would correspond to 0.6×10^{-5} g. A load of 0.3 g. could be safely used, so that for a sorption value of 1% on the weight of the sorbent, an extension corresponding to 0.003 g. i.e. an extension equal to .003 x 12.69 cm. or 0.038 cm. is measured. Since the possible error in this measurement is 0.002 cm. the percentage error in measuring as low a sorption value of 1% is about 5%. Since the expected sorption will not be less than about 3%,

errors of the order of 1.6% could at the most be expected. This is quite accurate for the purposes of our experiments.

(ii) The need for a high vacuum

Since sorption is mainly a surface phenomenon, the cleaning of the surface of the sorbent prior to any sorption experiment is of the utmost importance. Very small impurities of sorbed gases in the sorbent material are known to alter the course of sorption materially. Thus McBain (81) observed that the curve of the sorption isotherms for many gases on active charcoal were very different for sorbents cleaned under low vacuum compared with those cleaned under high vacuum. This will be readily appreciated when one remembers that most sorbates show an exponental variation of sorption with pressure. The simplest and the classical relationship between the quantity of sorbate sorbed and the pressure of the gas is given by Freundlich's equation

$$x/m = k.\, p^{\frac{1}{n}} \quad \ldots\ldots\ldots\

given value of sorption, the pressure would have to be reduced 32-fold. To reduce a given value of $^{x}/_{m}$ to 0.1% of its previous value, the pressure will have to be reduced 10^{15}-fold, and so on. The higher the evacuation, therefore, the better are the chances for thorough cleaning of the surface.

An Edwards "Speedivac"⊗ rotary pump was used to give a vacuum of 0.01 to 0.05 mm. This pump served as a backing pump to a mercury diffusion pump. Two kinds of diffusion pump were used. In preliminary experiments, an ordinary diffusion pump made of glass was used. This, however, never worked very satisfactorily. Vacua lower than .001 mm. were never attained. Later this was replaced by an Edwards two-stage mercury diffusion pump (all metal). This worked very well and vacua as low as 0.5×10^{-5} mm. were attained if due precautions were taken.

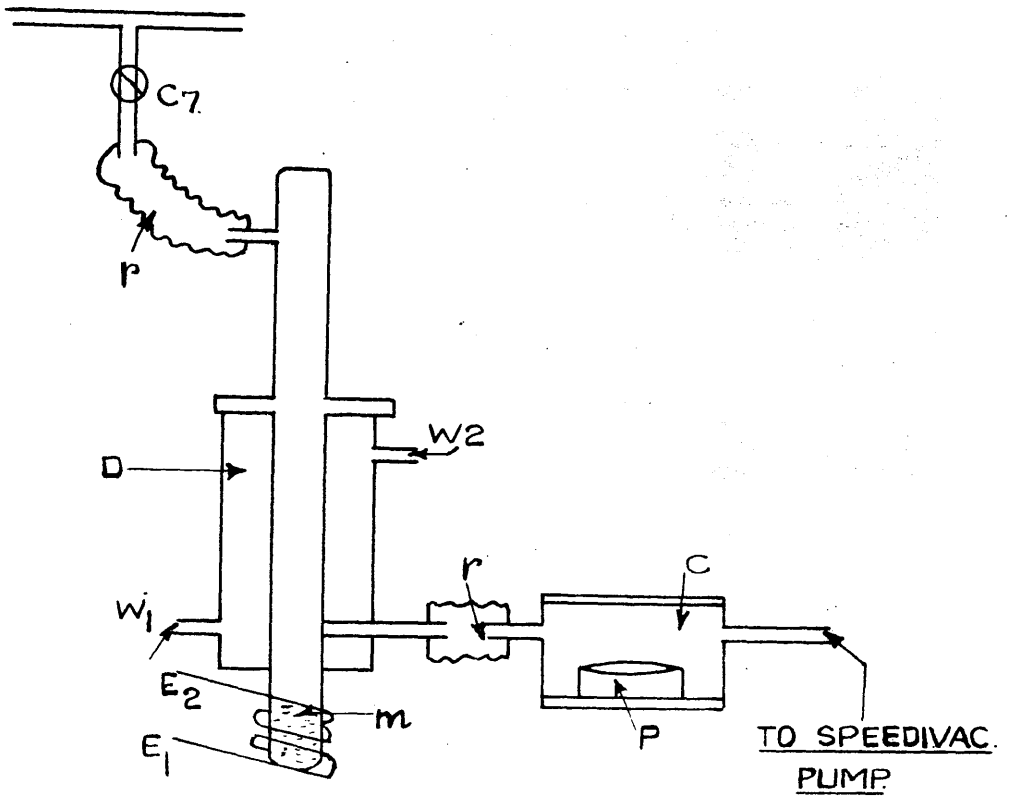
High vacuum technique

Some important precautions taken will be very briefly described.

(1) It was very necessary for the speed of evacuation to be fairly rapid. Glass tubing of great length or small bore was avoided.

(2) All joints and stop cocks in the system were of special high vacuum type.

⊗ The vacuum system is shown in Fig. 74 overleaf.



r = RUBBER CONNECTIONS.

D = DIFFUSION PUMP (EDWARD. 2 STAGE.)

W_1 = COOLING WATER INLET.

E_1-E_2 = ELECTRICAL HEATING COIL.

P = POT FOR HOLDING PHOSPHOROUS PENTOXIDE.

C = CONTAINER FOR POT P. (VACUUM TIGHT.)

m = MERCURY.

FIG:-74 SHOWING

THE VACUUM SYSTEM.

(3) The surfaces of the cocks and joints were thoroughly cleaned before grease was applied to them.

(4) A very thin layer of special high vacuum 'Silicone' grease was carefully applied by rubbing the grease on the thumb and the first fingers of the hand and moving them longitudinally on the stopcocks. This was found to be the best method of ensuring that the grease was applied uniformly.

(5) There were no rubber joints in the apparatus, right up to the high vacuum connection of the diffusion pump. The diffusion pump was connected to the apparatus by means of a rubber tube, previously boiled in a 10% solution of sodium hydroxide, then washed, dried, and coated with molten "Picein" wax.

The measurement of the high vacuum was made on the McLeod gauge. Fig. (31B) is a diagram illustrating the principle on which the gauge works. The end A of the glass tube T is connected to the vacuum. The bulb B, with the capillary of uniform bore (c) is connected to the mercury reservoir R and the tube T, as shown. A by-pass to tube T consists of a capillary arm p, having the same diameter as the capillary c. The reservoir R can be moved up and down over the connecting tube T.

At the start, the reservoir is so placed that when vacuum is applied, the mercury takes the level L.

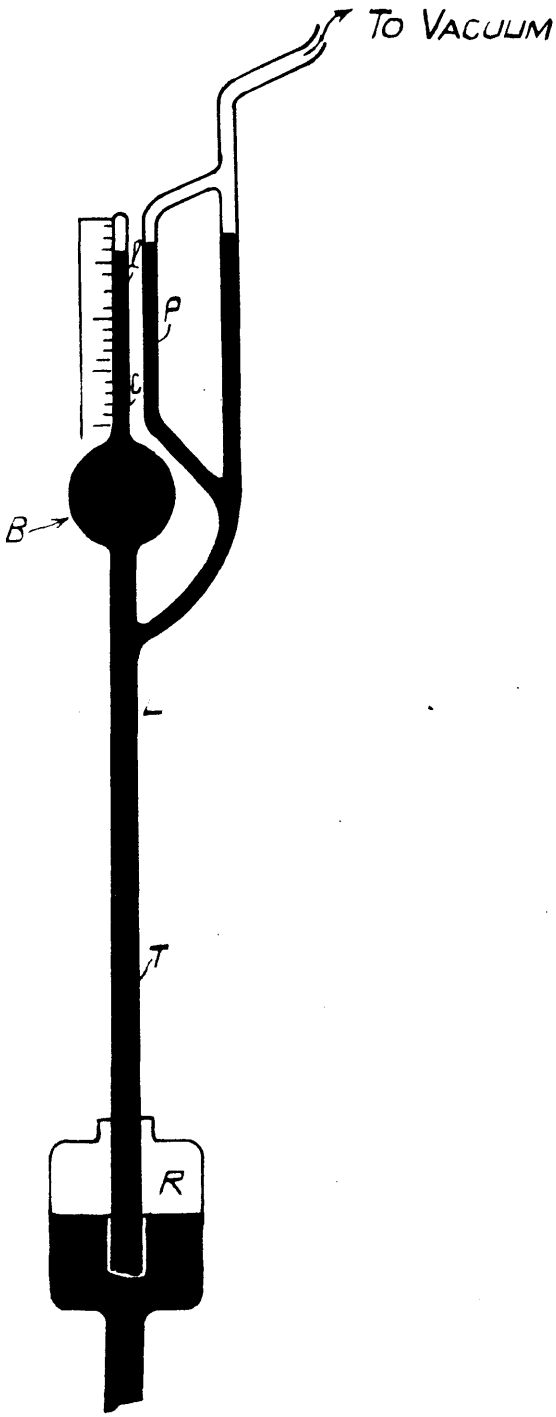


FIG. 31B

McLEOD GAUGE

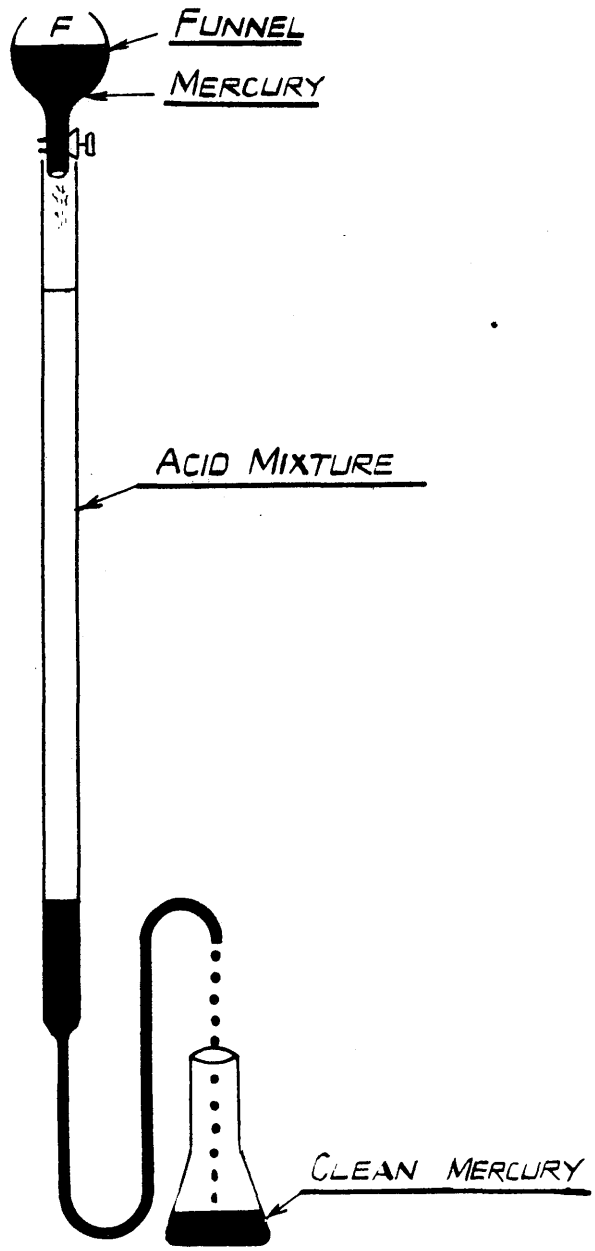


FIG. 31C.

SYSTEM FOR CLEANING MERCURY

Materials and Methods

To take a reading, the mercury reservoir is raised so that a known volume v of the residual gas in the system is cut off and compressed in the bulb B. The manometer is calibrated for different pressures previously. When the mercury reaches the level L in the arm p, the difference in level between L and the level of mercury in the capillary in p, gives a measure of the vacuum attained. McLeod gauges calibrated for various pressure ranges are available. The one used in these experiments had a range from 0.1 mm. to 0.1 x 10^{-6} mm.

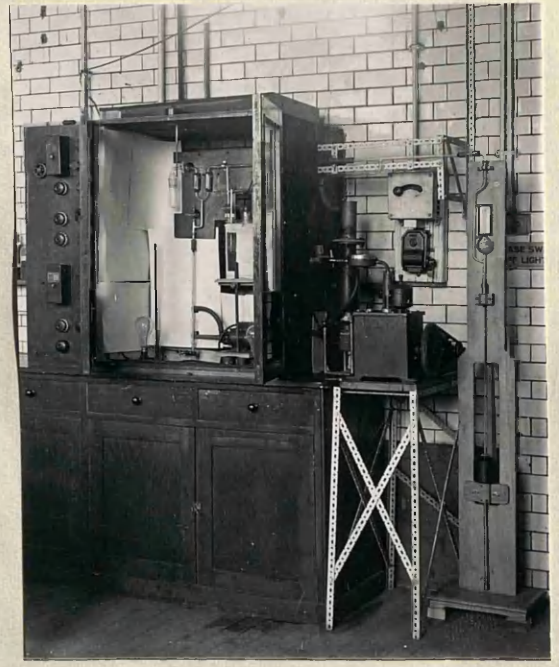
It is essential that specially cleaned mercury be used in the gauge. Dry mercury was cleaned in a mixture of nitric and sulphuric acids. Ostwald's simple technique was used (Fig.31C). Mercury was fed through the funnel F to an acid mixture contained in a burette connected with a capillary as shown. During passage through the acid mixture, metallic contaminents are dissolved and fairly pure mercury falls down the capillary. The mercury thus cleaned was further purified by distilling under vacuum.

There is one important point worth mentioning regarding the attainment and maintenance of high vacuum. The walls of the glass tubing in the apparatus keep on evolving gases and it is very essential for the pump system to evacuate these occluded

gases before a really good vacuum is attained. Further, since a McLeod gauge is used for measuring the vacuum, the existence of easily condensible gases inside the apparatus might sometimes be misleading. As, however, the connecting tubing in the apparatus was rather too long, there was no way of ensuring that all con-:densible vapours were necessarily removed. Before every set of experiments was started, the glass tubing in the apparatus was heated by moving a small flame over it. It was assumed that this practically removed condensible gases.

Another important consideration in the general experimental technique is the control of temperature. The quantity of vapour sorbed is not only a function of pressure but also of temperature. It is therefore essential for the liquid reservoir, the manometer and the sorption tube to be kept at constant temperature. Suit-:able thermostatic controls were therefore provided.

The actual apparatus used depended on whether the sorption was to be studied at or near the room temperature or at very much higher temperatures. At the lower temperatures it was possible to keep the liquid reservoir at one temperature by surrounding the whole assembly in an air thermostat (see photograph plate 1). The sorption tube was surrounded by a water thermostat whose



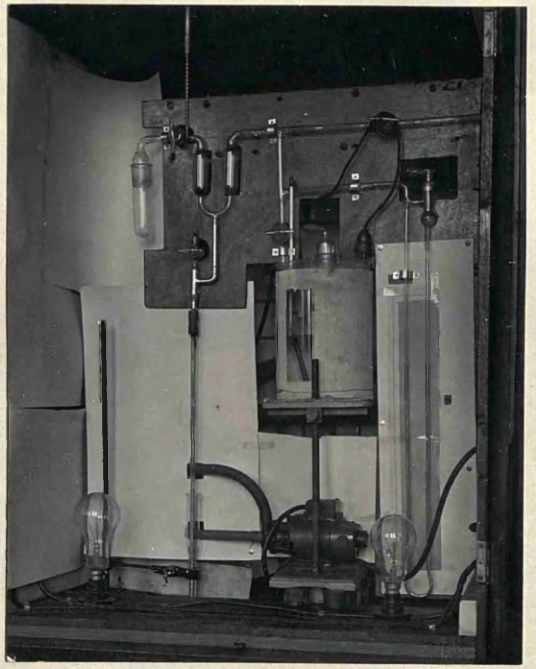


Plate I.

General view of Sorption apparatus.

Left: Vacuum system, air thermostat and the switchboard.

Right: Close up, showing the sorption system.

temperature was equal to or higher than that of the air thermostat. This enabled the effect of varying temperatures at constant pressures to be studied.

When sorptions at higher temperatures were to be studied, it was not possible to keep the sorbent and sorbate at different temperatures. In this case, both the liquid reservoir and the sorption tube were immersed in a paraffin bath electrically heated and thermostatically controlled. The two types of apparatus and the procedure for carrying out the experiments will be described under separate headings.

Apparatus and procedure for the determination of sorption at low temperatures

The apparatus:

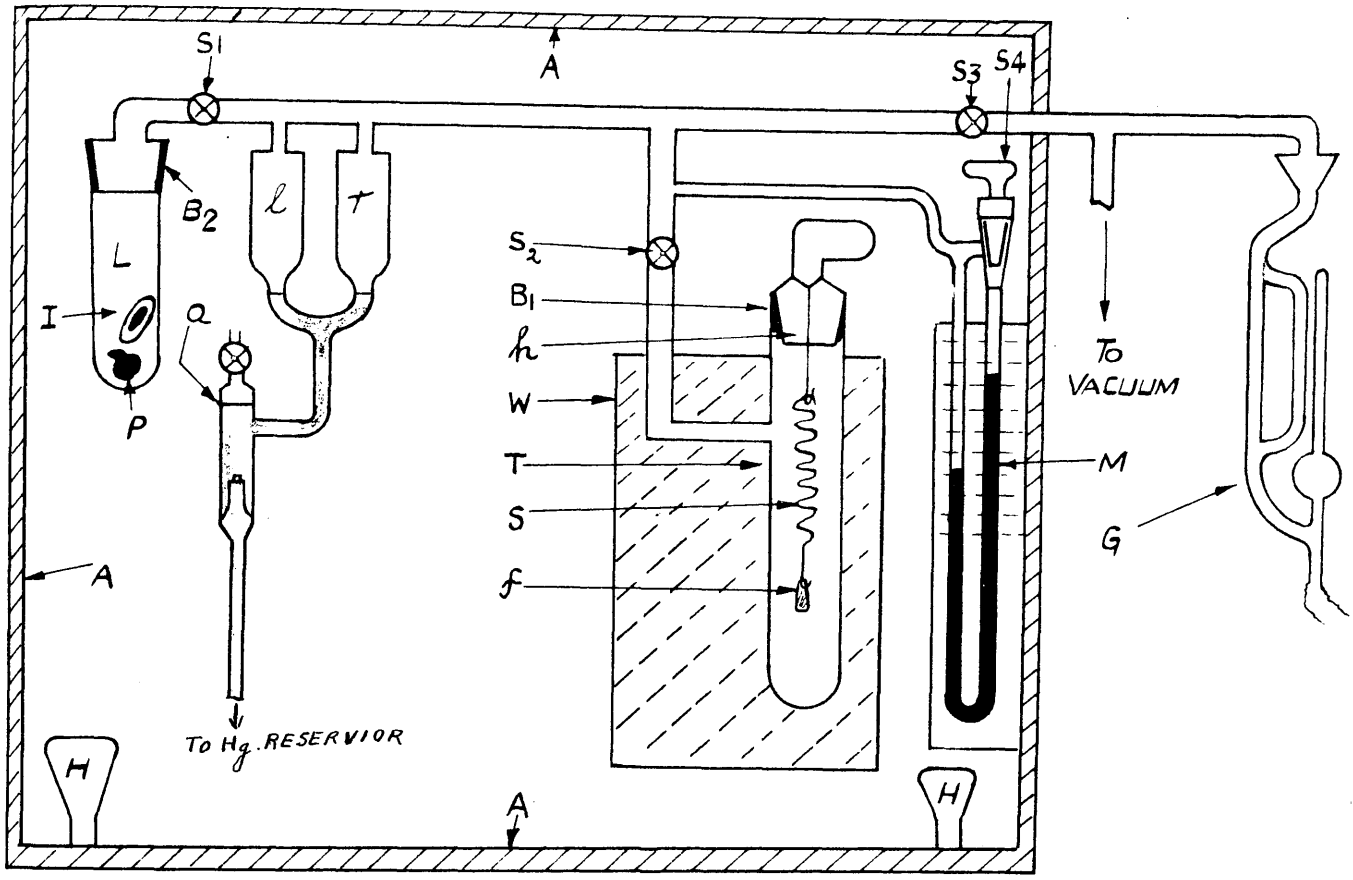
A diagrammatic sketch of the apparatus is shown in Fig.(31d). The actual photograph is shown in plate I.

It will be noticed from the photograph that the whole apparatus is mounted rigidly on the wall. The glass assembly is fixed on a wooden support S, which is screwed rigidly on "Ecofix" bars and angles fixed in the wall. This rigid mounting of the apparatus was necessary to avoid vibrations.

The glass assembly consists of:-

(i) The liquid reservoir L.

(ii) The mercury cut-off valve V, carrying the two limbs l



L = LIQUID RESERVOIR, V; MERCURY CUTOFF VALVE

ℓ, T = LIMBS OF MERCURY CUT OFF VALVE; a = AIR TRAP

R = MOVABLE MERCURY RESERVOIR

T = SORPTION TUBE

W = WATER THERMOSTAT

M = MANOMETER

A = AIR THERMOSTAT

P = THIN WALLED GLASS PHIAL

S1-S4 = STOPCOCKS

B1, B2 = GROUND GLASS JOINTS

S = SPIRAL

f = FIBRE SAMPLE

i = PIECE OF IRON ENCLOSED IN GLASS.

H = HEATING LAMPS

V = MERCURY CUT OFFVALVE

FIG. 31d

SORPTION APPARATUS FOR LOW TEMPERATURES

and r, and provided with an airtrap 'a' and a moveable mercury reservoir R.

(iii) The sorption tube T, surrounded by a water thermostat W.

(iv) The manometer M, and

(v) The air thermostat 'A' which houses the whole assembly, including the water thermostat.

(i) The liquid reservoir L is made from $1\frac{1}{4}$" diameter Pyrex glass tubing and carries a B-34 female joint at one end. At the extreme left end of the vacuum line is shown the B-34 male joint which is permanently joined to it. The reservoir could therefore be replaced at will.

The reservoir L is shown carrying a small thin-walled glass phial 'p' and a small piece of iron 'i' enclosed in glass. The glass phial carries the substance under study. The piece of iron can be lifted by a horse-shoe magnet and made to fall on and break the glass phial, when desired to introduce the substance under study into the evacuated assembly.

(ii) The mercury cut-off valve V serves a dual purpose. When the apparatus is evacuated, the mercury level rises and fills the valve and its lower limb as shown by the shaded portion. The valve is provided with an air trap as shown. Any small leakages

would thus not upset the vacuum in the main assembly. The valve V can be used to cut off the liquid reservoir from the rest of the apparatus by suitably raising the mercury reservoir R. Secondly it can also be used to take a measured quantity of the vapour into the right hand portion of the apparatus. The mercury level is first adjusted so that the mercury touches the bottom level in the limbs l and r. The vapour from the liquid reservoir L is then introduced into the left hand limb 'l' by opening the stop cock S_1. S_1 is then closed again and the reservoir R is then lowered a few inches so that the mercury level falls and connects the limb r with l. Thus the small quantity of vapour in l expands and fills the whole apparatus. The level of mercury is again raised and the limb r is thus cut off. The volume of 'l' is about 1/10th the volume of the sorption tube T, so that very little quantities of gas were able to be introduced successively into the sorption tube.

(iii) The sorption tube T is about 9" long and $1\frac{1}{2}$" wide. It carries a ground glass joint B_{14}, the male portion of which is re-:movable. The spring 's' carrying the fibre 'f' (about 0.15 to 0.25 g.) is hooked on to the male joint as shown. The fibre and the spring could be introduced or taken out by handling the male joint only. It is not necessary to remove the water thermostat

every time the spring is taken out.

(iv) The manometer M consists of a U-tube of 5 mm. bore. It carries a one-way valve S_4, of a special type. The top end of the valve contains a cavity into which mercury can be poured, and a liquid seal could thus be provided to ensure that there was absolutely no leakage into the right hand limb of the manometer once S_5 was closed.

The water thermostat is heated by means of a 750-watt electrical heater connected through a thermo switch and a "Sunvic" control unit. Neither the heater nor the thermoregulator are shown in the Figure.

(v) The air thermostat A encloses the whole assembly. Its front doors are of glass and the rest is of wood. A suitable air duct and a circulating fan are provided for the proper mixing of the air inside. The heating is done by four lamps H provided at the four corners of the wooden casing. The lamp heaters H were connected to the mains through "Sunvic" relay switch and a thermoregulator. These also are not shown in the diagrammatic sketch. Whenever the temperature of the liquid thermostat and the air thermostat were the same there was no difficulty in controlling the temperature. But whenever there was a marked difference in temperature between the two thermostats, e.g. 45°C.

for the water thermostat and 25°C. for the air thermostat, the heat of the water thermostat tended to increase the temperature of the air thermostat. This difficulty was avoided by providing suitable 'air-holes' in the sides of the air thermostat. A controlled quantity of cold air was thus introduced to counteract the heating effect due to the water thermostat.

The Procedure

Adjust the air thermostat and the water thermostat to the desired temperatures and start the thermostats and the fan. Clean all the ground glass joints and the stop cocks. Clean the liquid reservoir and dry the joints, the stop cocks and the liquid reservoir. Apply high vacuum silicone grease on all the stop cocks and put them in their places. Check for absence of leakages (by means of electronic leak-tester) before each experiment is started.

From a thin-walled soda glass tube (2 mm. dia.), blow a small glass bulb and fill it with the liquid to be studied, then seal it at both ends. Place the piece of iron 'i' and the glass phial 'p' inside the liquid reservoir. Apply grease to the male joint of B_2 and insert the liquid reservoir on it. Take about 0.2 g. of the fibre under study and make into a small loop. Make the loop as loose as possible. Attach it to the lower end of

the calibrated spring 's'. Hang the spring on to the male end of B_2, which is previously greased. Introduce the spring and the fibre into the tube and close B_2 properly by turning it round.

Keep all the stop cocks (S_1 to S_4) open and start the backing pump. When the expected vacuum (0.01 mm.) is attained, start the diffusion pump. The minimum vacuum attained should be 0.0001 mm.

The degassing is continued at the temperature of the experiment for four hours. After this there was no loss in weight of the fibre.

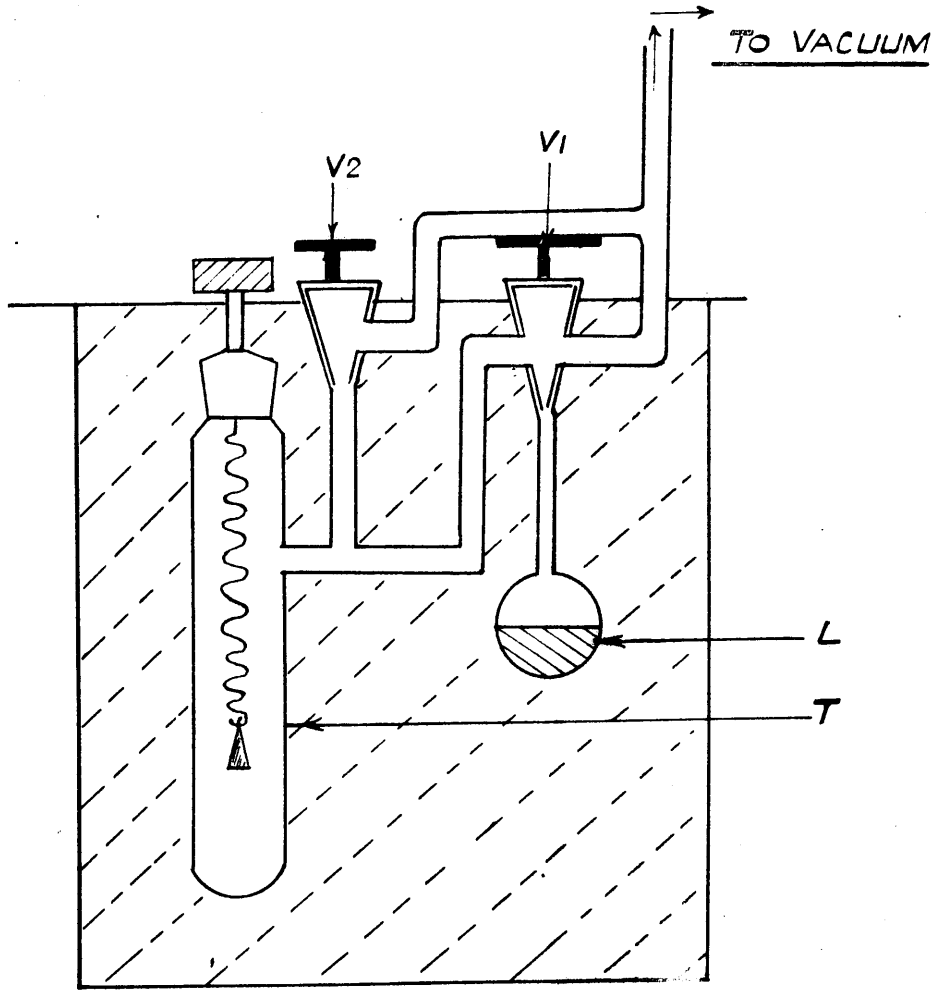
Close S_4 and S_3. Raise R so that the mercury in the cut-off valve V rises to the lower ends of the limbs l and r. Close S_1. Break the phial 'p' by raising 'i' by means of an electro magnet and allowing it to fall on to the phial. Open S_1 and take vapours into l. After equilibrium has been attained, close S_1. Close S_3. Lower R so that vapours from l fill r and the rest of the apparatus, except the sorption tube. Raise R again to cut off 'l' from the sorption region of the apparatus. Open S_3 so that the vapours expand into T. The volumes of l, r and the sorption tube were so designed that very small quantities of vapour could be taken into the sorption tube each time. It was thus possible to work at pressures up to the saturation value.

When rates are to be measured the length of the spiral is read by the cathetometer at desired intervals of time. When the equilibrium values are to be measured, sufficient time is allowed before the readings are taken.

Procedure for the measurement of high temperature adsorptions

The apparatus used is shown in Fig. (31e). The thermostatic bath was a six-litre Pyrex beaker containing liquid paraffin. A 1500-watt immersion heater was used for heating the liquid. The bath was well lagged with three layers of asbestos sheet. A "Sunvic" thermoregulator coupled to a high-vacuum switch was used for controlling the temperature. The paraffin oil is circulated by means of a Stewart Turner $\frac{1}{8}$ H.P. motor driving a centrifugal pump direct, and having metal tube connection for inlet and outlet.

T is the sorption tube carrying the spring and the fibre under study. L is the liquid reservoir. V_1 is a three-way tap connected as shown in the Figure. It could be evacuated separately and could be connected to the sorption tube independently. The purpose of the two-way tap V_2 is to allow evacuation of the fibre when the connection between the liquid bulb and the fibre is broken by closing the tap V_1.



L = LIQUID RESERVOIR
T = SORTION TUBE
V_1 = THREE WAY TAP
V_2 = TWO WAY TAP

FIG. 31e

SORPTION APPARATUS FOR HIGH TEMPERATURES

Procedure

Adjust the thermostat at the desired temperature and cali-:brate the spring by measuring the length under known loads. Take the apparatus out of the bath and cool and clean from out-:side. Through V_1, insert the liquid under study (or the solid) taking care that no particles adhere to the sides of the valve. If the substance is a compound like acetic acid which could vap-:ourise too easily in vacuum, the liquid bulb ~~was~~ is cooled in a freezing mixture and then evacuated to remove all air. The valve V_1 is then closed. (The male portion of the joint is of course properly greased as usual).

The sample of fibre under study is then hung on the spring and the apparatus is inserted into the paraffin bath once again, taking care that the level of the oil is well above that of the sorption tube and the top parts of the male joints of V_1 and V_2, as shown in the Figure. Valve V_2 is now opened and the fibre degassed at the temperature of the experiment, under high vacuum (0.0001 mm.). Two to three hours was quite sufficient for de-:gassing at the higher temperatures. The reading of the spiral to show the weight of the degassed fibre was taken, V_2 was closed and a connection between L and T made by suitably opening the valve V_1. The change in length of the spiral was ascertained

from time to time by cathetometer measurement.

The grease used was Edwards' high vacuum Silicone grease, which is stable up to 400°C. The empty space on top of the male joints of V_1 and V_2 was filled with the hot paraffin oil, which provided a liquid seal and kept the covers of the male joints at the same temperature as that of the liquid in the bath.

Appendix 3.

(a) Nylon yarn used as Sorbate:-

It has been discovered that the drawn nylon yarn used (40 den./15 fil.), contains a small amount of finely dispersed titanium dioxide.

Whether this would affect the experimental results, is very doubtful. A few cross-checkings, however, on bright nylon yarn of the same specification and not containing any titanium dioxide will be necessary to confirm that the delustring agent is without effect on the results. At the time of writing, a similar bright nylon yarn is not available and hence the work must be postponed.

(b) Some unsuccessful experiments:-

(i) Use of glass spiral for measuring sorption from solutions.

It was hoped that if the glass spiral could be used for measuring sorptions from solution, it would provide a new and quick method of sorption study. If successful, this would be of much value in experimental dyeing investigations. In spite of many trials, however, it was discovered that there are many difficulties involved in this application. For instance, the buoyancy effects noticed during calibration of the spiral were entirely different for metal weights from those observed when a fibre sample was used. Moreover, the wetting of the fibre takes some time and it is difficult to decide what exactly is its

dry weight prior to the start of adsorption. Furthermore, the spiral position is affected by very small currents within the solution surrounding it and the taking of readings is therefore extremely difficult.

The use of this method was therefore not pursued further.

(ii) Several experiments were made to determine the absorption of hydrochloric acid from aqueous solution on drawn nylon fibre at pH values of about 1.0 . No absorption at all could be detected. This is completely at variance with the results of Lemin and Vickerstaff (26) and of Boulton (27). Boulton, however, used sulphuric acid. This matter obviously requires further investigation. It is consistent with the non-absorption of benzene sulphonic acid reported elsewhere in this thesis.

(c) Amino group content of nylon:-

A determination of the free amino-group content of the drawn nylon fibre was made, by using van Slyke's reagent. The result was of the order of 0.026 milliequivalents per gm., but it is not believed that the particular experiments gave high accuracy, though they did definitely give a positive result.

This figure is consistent with Lemin et al's value for mineral acid absorption, but not, of course, with our observation that strong acids are unabsorbed. This, again, will need further investigation.

APPENDIX 4

TABULATED RESULTS.

Table 1.

isotherm for Aqueous Phenol on Drawn nylon at 25°C			
Orig.conc.of solution %	Equilibrium Concentration C_e %	Relative Concentration C_R cc/Solubility	Amt.sorbed at Equilibrium C_F m.mol/gm.
0.5	0.43	0.0505	0.79
1.0	0.83	0.0975	0.91
1.5	1.13	0.1327	1.32
2.0	1.41	0.1656	1.57
2.5	1.69	0.1985	1.74
3.0	1.79	0.2102	2.15

Table 2.

isotherm for Aqueous Phenol on Drawn nylon at 40°C			
Orig.conc. %	Equilibrium Concentration C_e %	Relative Concentration C_R	Amt.sorbed at Equilibrium C_F m.mol./gm.
0.25	0.22	0.0228	0.58
0.5	0.42	0.0435	0.81
1.0	0.77	0.0798	1.21
1.5	1.10	0.1140	1.42
2.0	1.28	0.1326	1.92
2.5	1.55	0.1606	2.03
3.0	1.74	0.1803	2.24

Table 3.

isotherm for Aqueous Phenol on Drawn nylon at 60°C			
Orig.conc. %	Equilibrium Concentration C_e %	Relative Concentration C_R	Amt.sorbed at Equilibrium C_F m.mol./gm.
0.5	0.43	0.0308	0.65
1.0	0.83	0.0595	0.91
1.5	1.15	0.0824	1.24
2.0	1.45	0.1034	1.46
2.5	1.68	0.1203	1.74
3.0	1.90	0.1361	1.96

Table 4.

isotherm for Aqueous Phenol on undrawn nylon at 25°C

Original concentration %	Equilibrium concentration C_e %	Relative concentration C_R	Amount sorbed at equilibrium m.mol./gm. C_F
0.25	0.23	0.0270	0.40
0.50	0.43	0.051	0.70
1.00	0.80	0.094	1.06
1.50	1.05	0.117	1.54
2.00	1.29	0.152	1.86
2.50	1.36	0.160	2.43
3.00	1.48	0.174	2.66

Table 5.

isotherm for Aqueous Phenol on undrawn nylon at 40°C

Original concentration %	Equilibrium concentration C_e %	Relative concentration C_R	Sorption m.mol./g. C_F
0.25	0.21	0.0218	0.85
0.50	0.40	0.0415	1.06
1.00	0.74	0.0767	1.46
1.50	1.00	0.1036	1.78
2.00	1.27	0.1316	2.00
2.50	1.49	0.1545	2.13
3.00	1.65	0.1710	2.40

Table 6.

isotherm for Aqueous Phenol on undrawn nylon at 60°C

Original concentration %	Equilibrium concentration C_e %	Relative concentration C_R	Sorption m.mol./g. C_F
0.25	0.22	0.0122	0.55
0.50	0.43	0.0258	0.79
1.00	0.78	0.0467	1.17
1.50	1.07	0.0640	1.32
2.00	1.37	0.0823	1.67
2.50	1.67	0.100	1.99
3.00	1.82	0.109	2.11

Table 8.

Thermal expansion coefficients of various materials.

Material	Exp.Coeff. x 10^7
Monax Glass	36.0
Pyrex Glass	32.0
Platinum	91.0
Tungsten	47.0
Copper	162.0
Quartz	5.8

Table 10

isotherm for Aqueous Resorcinol on Drawn Nylon at 25°C

Equilibrium Concentration C_e %	Relative Concentration C_R	Sorption m.mol/gm. C_F
0.368	0.0055	0.511
0.719	0.0107	0.660
0.948	0.0142	0.727
1.410	0.0210	0.791
1.963	0.0293	0.938
2.548	0.0380	1.282
3.410	0.0509	1.645
4.024	0.0602	1.954
5.200	0.0776	2.068
7.700	0.1150	2.581
9.500	0.1420	2.945

Table 11.

isotherm for Aqueous Resorcinol on Undrawn Nylon at 25°C

Equilibrium Concentration C_e %	Relative Concentration C_R	Sorption m.mol/gm. C_F
0.676	0.0101	1.38
0.989	0.0148	1.54
1.673	0.0250	1.41
2.067	0.0309	1.63
2.750	0.0410	1.70
4.070	0.0607	1.92
7.778	0.1160	2.74
12.530	0.1869	3.37

Table 12.

isotherm for Aqueous Aniline on Drawn Nylon at 25°C

Equilibrium Concentration C_e %	Relative Concentration C_R	Sorption m.mol/g. C_F
0.226	0.063	0.096
0.336	0.093	0.156
0.530	0.147	0.269
0.662	0.183	0.269
0.881	0.244	0.298
1.317	0.290	0.312
1.848	0.512	0.438

Table 13.

isotherm for Aqueous Aniline on Undrawn Nylon at 25°C

Equilibrium Concentration C_e	Relative Concentration C_R	Sorption m.mol/gm. C_F
0.130	0.036	0.082
0.189	0.052	0.087
0.349	0.097	0.148
0.601	0.166	0.269
0.950	0.264	0.385
1.089	0.302	0.528
1.697	0.471	0.817
2.169	0.602	0.971

Table 14.

Sorption isotherm for Aqueous Benzoic acid on Drawn Nylon at 25°C

Original Concentration %	Equilibrium Concentration C_e %	Sorption %	Sorption m.mol/g. C_F
0.100	0.073	1.34	0.110
0.125	0.089	1.46	0.120
0.150	0.100	1.67	0.137
0.175	0.115	1.78	0.146
0.200	0.122	1.96	0.160
0.225	0.129	2.14	0.175
0.250	0.136	2.30	0.188
0.275	0.144	2.37	0.195

Table 15.

Rate of sorption of Aqueous Phenol on Drawn Nylon at 25°, 40° and 60°C. Concentration of starting bath = 2%

25°C		40°C		60°C	
Time Hrs.	Sorption m.mol./g. C_F	Time Hrs.	Sorption m.mol./g. C_F	Time Hrs.	Sorption m.mol./g. C_F
2.0	1.20	1.00	1.17	1.75	1.46
3.5	1.65	2.25	1.40	2.50	1.46
5.5	1.74	3.25	1.58	4.50	1.56
7.0	1.74	4.25	1.58	5.50	1.56
		5.25	1.58	6.75	1.56

Table 16.

Rate of sorption of Aqueous Phenol on Drawn Nylon at 25°,40° and 60°C. Concentration of starting bath=2.5%

25°C		40°C		60°C	
Time Hrs.	Sorption m.mol./g. C_F	Time Hrs.	Sorption m.mol./g. C_F	Time Hrs.	Sorption m.mol./g. C_F
2.0	1.70	1.0	1.25	2.0	1.32
3.0	1.92	3.0	1.58	3.0	1.68
5.0	2.05	4.0	1.70	4.5	1.76
6.0	2.05	5.5	1.70	5.5	1.76
		6.5	1.79	7.0	1.76

Table 17.

Rate of sorption of Aqueous Phenol on Drawn Nylon at 25°, 40°and 60°C. Concentration of starting bath = 3.0%

25°C		40°C		60°C	
Time Hrs.	Sorption m.mol./g. C_F	Time Hrs.	Sorption m.mol./g. C_F	Time Hrs.	Sorption m.mol./g. C_F
2.0	1.86	1.0	1.64	1.0	1.84
3.5	2.05	3.0	1.79	3.0	1.90
5.5	2.22	4.0	1.93	4.5	1.90
7.0	2.27	5.5	2.05	5.5	1.90
		6.5	2.05	7.0	1.95

Table 18.

Rate of sorption of Aqueous Phenol on Undrawn Nylon at 25°C, 40° and 60°C. Concentration of starting bath = 2.0 %

25°C		40°C		60°C	
Time Hrs.	Sorption m.mol./gm. C_F	Time Hrs.	Sorption m.mol./gm. C_F	Time Hrs.	Sorption m.mol./gm. C_F
1.0	0.34	1.0	0.81	1.5	1.52
2.0	0.48	3.0	1.32	2.5	1.52
3.0	0.60	4.0	1.60	4.5	1.68
4.0	0.86	5.5	1.86	5.5	1.76
5.0	0.94	6.5	1.86	6.5	1.62
6.0	1.06				

Table 19.

Rate of sorption of Aqueous Phenol on Undrawn Nylon at 25°, 40° and 60°C. Concentration of starting bath = 2.5 %

25°C		40°C		60°C	
Time Hrs.	Sorption m.mol./gm. C_F	Time Hrs.	Sorption m.mol./gm. C_F	Time Hrs.	Sorption m.mol./gm. C_F
2.0	0.85	1.0	1.17	1.5	1.70
4.5	1.28	2.25	1.81	2.5	1.92
5.75	1.60	3.25	1.92	4.5	1.92
6.75	1.70	4.25	1.96	5.5	1.92
		5.25	1.98	6.75	1.99

Table 20.

Rate of sorption of Aqueous Phenol on Undrawn Nylon at 25°, 40° and 60°C. Concentration of starting bath = 3.0 %

25°C		40°C		60°C	
Time Hrs.	Sorption m.mol./gm. C_F	Time Hrs.	Sorption m.mol./gm. C_F	Time Hrs.	Sorption m.mol./gm. C_F
1.0	0.49	1.0	1.54	1.5	1.86
2.0	1.02	3.0	2.13	2.5	1.86
3.5	1.96	4.0	2.24	4.5	2.05
4.5	2.27	5.5	2.40	5.5	2.05
5.5	2.40	6.5	2.48	6.75	2.14
6.5	2.66				

Table 23.

Rate of sorption of Benzoic acid (Aqueous) at various concentrations of starting bath and at 25°C, on Drawn Nylon.

Original Concentration %	Percentage Sorption				
	1 Hour	2 Hours	3 Hours	4 Hours	5 Hours
0.100	0.18	0.79	0.73	0.97	1.34
0.125	0.73	0.98	1.42	1.56	1.76
0.150	1.16	1.38	1.79	2.04	2.08
0.175	1.01	1.26	1.68	1.88	2.02
0.200	1.07	1.62	1.96		
0.225	1.38	1.74	2.30	2.35	2.35
0.250	1.44	2.00	2.26	2.42	2.45

Table 24.

Rate data for the sorption of Aqueous Benzoic acid on Drawn Nylon at 40°C and at three different concentrations.

Original Concentration	Percentage Sorption			
	50 Min.	1 Hour 50 min.	2 Hours 50 min.	4 Hours 50 min.
0.125	1.02	1.22	1.42	1.52
0.150	1.18	1.42	1.54	1.63
0.275	1.98	2.25	2.26	2.31

Table 26.

Spiral No.1	
Load gm.	Extension cm.
0.1	1.745
0.2	3.450
0.3	5.150
0.4	6.880
0.5	8.580

Table 27.

Spiral No.2	
Load gm.	Extension cm.
0.1	0.940
0.2	1.929
0.3	2.923
0.4	3.881
0.5	4.871

Table 29.

Rate of sorption of water vapour on drawn nylon at 26.5°C

Vap. press. = 8 m.m.			Vap. press. = 16 m.m.		
Time min.	% sorption	m.mols./g. C_F	Time min.	% sorbed	m.mols./g. C_F
2	0.866	0.482	4	1.590	0.885
3	1.300	0.722	10	2.128	1.184
5	1.540	0.833	15	2.500	1.390
20	1.732	0.962	20	2.771	1.540
40	1.732	0.962	30	3.050	1.690
			40	3.150	1.750

Table 30.

Rate of sorption of methyl alcohol vapour on drawn nylon at 26.5°C.

Vap.press.= 13.5 mm.			Vap.press.=36 mm.			Vap.press.= 94 mm.		
Time min.	%sorpt	m.mol/g C_F	time min	% sorb	m.mols/g C_F	time min	%sorbed	m.mol/g C_F
3	0.35	0.11	2	0.78	0.24	5	2.1	0.67
10	0.68	0.21	5	1.07	0.34	10	3.3	1.04
15	0.69	0.22	10	1.51	0.47	20	4.0	1.25
25	0.73	0.23	20	2.00	0.63	35	4.4	1.36
35	0.81	0.25	30	2.25	0.70	60	4.6	1.46
50	0.94	0.30	90	2.53	0.80			

Table 31.

Rate of sorption for ethyl alcohol on drawn nylon at 26.5°C		
time	sorption	sorption m.mols/g. C_F
10	0.69	0.15
34	1.84	0.40
46	2.17	0.45
70	2.53	0.55

Table 31 a.

Rate of Desorption for water and methyl alcohol on drawn nylon at 26°C.

Methyl alcohol		Water	
time t min.	Amount desorbed %	time t min.	Amount desorbed %
0	0	0	0
1	0.49	1	1.81
15	2.20	4	3.84
25	2.88	15	4.70
45	3.43	35	5.00
90	4.32		
120	4.41		

Table 32.

Rate of sorption of Phenol Vapour on Drawn Nylon at 25°C.
Extension of spiral = 12.69 cm./gm.

time t min.	spiral length cm.	Extension cm.	Amount adsorbed m.mol/g.	C_F
0	3.790	0.00	0.00	
2"	3.817	0.027	0.85	
8"	3.875	0.085	0.267	
15"	3.902	0.112	0.352	
45"	4.028	0.180	0.522	
90"	4.052	0.238	0.747	
150"	4.073	0.283	0.889	
210"	4.098	0.308	0.967	
270"	4.135	0.345	1.080	
315"	4.153	0.363	1.140	
345"	4.155	0.365	1.150	

Table 33.

Rate of sorption of Phenol Vapour on wool at 25°C
Extension of spiral = 13.80 cm./gm.

time t min.	spiral length cm.	Extension cm.	sorption m.mol/g.	C_F
0	6.033	0.00	0.00	
18	6.047	0.014	0.068	
40	6.052	0.019	0.093	
75	6.055	0.022	0.110	
80	6.060	0.027	0.132	
180	6.060	0.027	0.132	
293	6.060	0.027	0.132	
!	!	!	!	
!	!	!	!	
!	!	!	!	
31.5hrs	6.097	0.064	0.313	

Table 34.

Sorption of Phenol Vapour on Undrawn Nylon at 60°C
Extension of spiral = 8.5 cm./gm.

time t min.	length l cm.	extension cm.	sorption C_F m.mol./g.
0	7.052	0	0
2	7.082	0.030	0.373
7	7.089	0.032	0.398
11	7.103	0.051	0.633
22	7.107	0.055	0.683
32	7.116	0.064	0.795
52	7.125	0.073	0.907
80	7.175	0.123	1.530
160	7.216	0.164	2.030
215	7.227	0.175	2.180
255	7.280	0.228	2.830

Table 35.

Sorption of Phenol Vapour on Undrawn Nylon at 70°C
Extension of spiral = 9.06 cm./gm.

time t min.	length l cm.	extension cm.	sorption C_F m.mol./g.
	7.539	0	0
9	7.663	0.124	1.42
16	7.700	0.161	1.84
20	7.722	0.183	2.10
27	7.741	0.202	2.31
30	7.758	0.219	2.51
50	7.818	0.279	3.20
140	8.048	0.509	5.83

Table 36.

Sorption of Phenol Vapour on Undrawn Nylon at 80°C

Extension of spiral = 8.5 cm./gm.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol/g.
0	7.068	0 - 0	0 - 0
3	7.162	0.094	1.231
9	7.220	0.152	1.991
20	7.270	0.202	2.646
50	7.330	0.262	3.354
80	7.372	0.304	3.981
130	7.415	0.347	4.540
210	7.475	0.407	5.331

Table 37.

Sorption of Phenol Vapour on wool at 60°C
Extension of spiral = 8.4cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.925	0.0	0.0
3	6.950	0.025	0.352
11	6.970	0.045	0.658
20	7.000	0.075	1.047
60	7.033	0.108	1.508
120	7.055	0.130	1.774
180	7.050	0.125	1.744
480	7.195	0.245	3.422

Table 38.

Sorption of Phenol Vapour on wool at 70°C
Extension of spiral = 9.1 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C m.mol./g.
0	7.685	0.0	0.0
2.5	7.697	0.012	0.127
5.5	7.714	0.029	0.318
12.0	7.751	0.067	0.724
13	7.753	0.068	0.777
25	7.800	0.115	1.315
45	7.885	0.200	2.19
90	8.026	0.341	3.90
145	8.153	0.468	5.35

Table 39.

Sorption of Phenol Vapour on wool at 80°C
Extension of spiral = 8.4 cm.

time t min.	length l cm.	extension cm.	sorption C_p m.mol./g.
0	6.875	0.0	0.0
2	6.896	0.023	0.344
5	6.929	0.056	0.839
9	6.967	0.094	1.409
12	6.992	0.119	1.78
30	7.044	0.171	2.57
60	7.078	0.205	3.07
102	7.111	0.238	3.57
180	7.152	0.279	4.18
340	7.219	0.346	5.186

Table 40.

Sorption rate of Acetic acid Vapour on Undrawn Nylon at 25°C
Extension of spiral = 9.1 cm./g.

time t min	spiral length l cm.	extension cm.	sorption C_F m.mol./g
0	7.567	0.0	0.0
1	7.568	0.001	0.0068
2	7.575	0.008	0.054
5	7.585	0.018	0.122
10	7.590	0.023	0.157
30	7.605	0.038	0.206
65	7.605	0.048	0.327
230	7.639	0.073	0.497
260	7.685	0.128	0.875

Table 41.

Sorption rate of Acetic acid Vapour on Drawn Nylon at 25°C
Extension of spiral = 5.3 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	7.950	0.0	0.0
2.5	7.980	0.030	0.267
4	7.990	0.040	0.356
8	8.000	0.050	0.445
30	8.038	0.088	0.784
60	8.063	0.113	1.007
157	8.085	0.135	1.202

Table 42.

Sorption rate for Acetic acid Vapour on wool at 30°C
Extension of spiral = 13.8 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.317	0	0
3	6.468	0.151	1.018
5	6.541	0.224	1.510
8	6.617	0.300	2.022
11	6.678	0.360	2.433
15	6.721	0.414	2.791
20	6.775	0.459	3.094

Table 43.

Sorption rate for Acetic acid Vapour on wool at 40.5°C
Extension of spiral = 13.81 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.915	0	0
1	7.013	0.098	0.5182
2	7.082	0.167	0.8831
4	7.192	0.277	1.465
8	7.345	0.430	2.274
13	7.425	0.510	2.698
30	7.591	0.675	3.570
60	7.713	0.798	4.220
80	7.777	0.862	4.550

Table 44.

Sorption rate of Acetic acid Vapour on wool at 50.5°C
Extension of spiral = 13.81 cm./gm.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./gm.
0	6.992	0	0
1	7.130	0.1380	0.7166
2	7.228	0.236	1.243
4	7.335	0.343	1.806
8	7.472	0.480	2.527
15	7.585	0.593	3.123
30	7.685	0.693	3.649
60	7.795	0.803	4.228
90	7.835	0.843	4.438

Table 45.

Sorption rate for Acetic Acid Vapour on wool at 60.5°C
Extension of spiral = 13.81 cm./gm.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./gm.
0	7.750	0	0
1	7.950	0.200	0.978
2	8.045	0.295	1.443
3	8.120	0.370	1.809
4	8.175	0.425	2.079
6	8.258	0.508	2.485
10	8.380	0.630	3.081

Table 46.

Sorption rate of stabilised dry acetic acid on wool.
Temp. of acid = 28°C. Temp. of sorption = 30°C
Extension of spiral = 13.80 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.295	0	0
5	6.290	0	0
11	6.340	0.045	0.378
20	6.380	0.085	0.715
30	6.440	0.145	1.220
40	6.490	0.195	1.623

Table 47.

Sorption rate of stabilised dry acetic acid on wool.
Temp. of acid = 28°C. Temp. of sorption = 35°C
Extension of spiral = 13.80 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.865	0	0
3	6.880	0.015	0.0973
6	6.875	0.010	0.0658
11	6.880	0.015	0.0973
20	6.900	0.035	0.2303
30	6.917	0.052	0.3422
47	6.948	0.083	0.5462
60	6.972	0.107	0.7041

Table 48.

Sorption rate of stabilised dry acetic acid on wool.

Temp. of acid = 28°C. Sorption temp. = 45.3°C

Extension of spiral = 13.80 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.975	0	0
1	6.990	0.015	0.096
5	6.995	0.020	0.128
22	7.003	0.028	0.179
32	7.020	0.045	0.288
45	7.035	0.060	0.384
75	7.055	0.080	0.512
90	7.070	0.095	0.608

Table 49.

Sorption and desorption rate of stabilised dry acetic acid on wool.
Liquid temp. = 28°C. Sorbent temp. = 30°C
Extension of spiral = 13.85 cm./g.

Sorption		Desorption	
time t min.	sorption C_F m.mol/g	time t min.	sorption C_F m.mol./g.
0	0.0	0	2.077
1	0.221	3	1.863
3	0.547	13	1.530
7	0.918	23	1.391
10	1.136	33	1.275
33	2.077	60	1.113

Table 50.

Rate of sorption of dry hydrogen chloride on wool at 25°C.
Extension of spiral = 13.80 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	8.880		
3	8.880		
6	8.885		
10	8.890		
15	8.890		
30	8.885		
!			
!			
!			
270	8.890		

Table 52.

Sorption rate of ß-naphthol vapours on drawn nylon at 120°C

Extension of spiral = 14.00 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	7.545	0	0
1	7.615	0.070	0.217
3	7.665	0.120	0.372
6	7.700	0.155	0.480
11	7.755	0.210	0.650
15	7.785	0.240	0.744
24	7.850	0.305	0.945

Table 53.

Sorption rate of ß-naphthol vapours on undrawn nylon at 120°C.

Extension of spiral = 14.00 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m. mol./g.
0	7.385	0	0
1	7.400	0.015	0.0686
2	7.400	0.015	0.0686
5	7.405	0.020	0.0914
12	7.420	0.035	0.229
23	7.435	0.050	0.160
33	7.445	0.060	0.274

Table 54.

Sorption rate of ß-naphthol vapours on powdered nylon at 120°C.
Extension of spiral = 14.00 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.915	0	0
1	7.105	0.190	0.827
2	7.170	0.255	1.087
4	7.270	0.355	1.545
6	7.378	0.433	1.884
8	7.400	0.485	2.110
10	7.450	0.535	2.328
18	7.580	0.665	2.891
20	7.610	0.695	3.024

Table 55.

Sorption rate of ß-naphthol vapours on wool at 120°C
Extension of spiral = 14.00 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.480	0	0
1	6.493	0.0130	0.0747
3	6.493	0.0130	0.0747
10	6.493	0.0130	0.0747
25	6.493	0.0130	0.0747

Table 56.

Sorption rate of ß-naphthol vapours on wool at 130°C

Extension of spiral = 13.83 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.455	0	0
1	6.480	0.030	0.1857
4	6.490	0.035	0.2166
13	6.495	0.040	0.2476
20	6.507	0.052	0.3218
30	6.515	0.060	0.3714
135	6.530	0.075	0.4641

Table 57.

Sorption rate of ß-naphthol vapours on powdered nylon at 133°C

Extension of spiral = 14.00 cm./g

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	7.245	0	0
1	7.480	0.235	0.955
2	7.535	0.290	1.179
3	7.570	0.325	1.321
5	7.630	0.385	1.565
8	7.675	0.430	1.749
15	7.735	0.490	1.992
20	7.760	0.515	2.093
24	7.765	0.520	2.113

Table 58.

Sorption rate of ß-naphthol vapours on powdered nylon at 140°C

Extension of spiral = 13.83 cm./g.

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g.
0	6.900	0	0
1.5	7.210	0.310	1.122
2.5	7.282	0.382	1.741
4.5	7.390	0.490	2.233
9	7.565	0.665	3.031
10	7.620	0.720	3.281
12	7.675	0.775	3.532
15	7.750	0.850	3.874
20	7.855	0.955	4.352
42	8.130	1.230	5.607
75	8.175	1.275	5.811

Table 59.

Sorption-desorption cycles for ß-naphthol vapour on undrawn nylon at 120°C

time t min.	sorption C_F m.mol./g.	time t min.	sorption C_F m.mol./g.
	1st. sorption		1st. desorption
0	0.	0	0.274
1	0.0686	2	0.229
2	0.0686	5	0.183
5	0.0914	60	0.137
12	0.160	102	0.115
23	0.229		
33	0.274		
	2nd. sorption		2nd. desorption
0	0.115	0	1.117
3	0.319	3	0.937
12	0.411	15	0.777
35	0.846	47	0.549
45	0.983	60	0.526
60	1.117	100	0.411
	3rd. sorption		3rd. desorption
0	0.410	0	3.680
3	1.302	2	3.154
11	2.354	70	1.165
18	2.992	130	0.960
30	3.680		
	4th. sorption		-----
0	0.960		
3	2.125		
6	2.651		
10	3.817		
20	6.628		
45	10.030		

Table 60.

Sorption-desorption cycles for ß-naphthol on drawn nylon at 120°C.

time t min.	sorption C_F m.mol/g.	time t min.	sorption C_F m.mol/g.
1st. sorption		1st. desorption	
0	0	0	0.945
1	0.217	20	0.852
3	0.372	150	0.387
6	0.480		
11	0.650		
15	0.744		
24	0.945		
2nd. sorption		2nd. desorption	
0	0.387	0	2.401
1	1.285	1	2.15
3	1.595	3	2.15
7	1.905	30	1.518
11	2.401		

Table 61.

Sorption-desorption cycle for ß-naphthol on powdered nylon at 120°C

time t min.	sorption C_F m.mol./g.	time t min.	sorption C_F m.mol./g.
0	0	0	3.024
1	.827	1.5	2.828
2	1.087	15	2.154
4	1.545	"	
6	1.884	"	
8	2.110	"	
10	2.328	"	
18	2.891	40	1.435
20	3.024		
2nd. sorption			
0	1.435		
2	2.502		
6	3.220		
9	3.556		
13	4.003		

Table 62.

Sorption-desorption cycles for ß-naphthol on wool at 120°C

time t min.	sorption C_F m.mol./g.	time t min.	sorption C_F m.mol/g.
1st. sorption		1st. desorption	
0	0	0	0.0747
1	0.0747	5	0.000
3	0.0747		
10	0.0747		
25	0.0747	10	0.000
2nd. sorption		2nd. desorption	
0	0	0	1.379
2	0.2299	2	1.207
4	0.223	12	1.035
12	0.376	23	0.891
63	1.035	60	0.862
93	1.235	80	0.804
120	1.379	120	0.747
3rd. sorption		3rd. desorption	
0	0.749	0	1.695
2	0.977	3	1.408
4	1.109	8	1.263
10	1.293	21	1.091
20	1.494	45	1.006
40	1.638	60	1.006
60	1.695	90	0.919
		180	0.862
4th. sorption		------	
0	0.862		
2	1.035		
6	1.120		
12	1.264		
30	1.638		
102	1.896		

Table 63.

Sorption and desorption cycle for benzoic acid on powdered nylon at 130°C.

time t min.	sorption C_F m.mols/g	time t min.	sorption C_F m.mol./g.
	1st. sorption		2nd. desorption
0	0	0	0.743
5	0.116		
12	0.232	12	0.255
23	0.302	42	0.175
35	0.395	62	0.000
75	0.534		
150	0.743		
	2nd. sorption		2nd. desorption
0	0	0	0.840
2	0.626	10	0.750
12	0.812	90	0.375
29	0.905	130	0.240
65	1.253	180	0.000
92	1.579		
112	1.579		
130	1.509		
144	1.346		
167	0.840		

Table 64.

Sorption & desorption cycle for benzoic acid vapour on wool at 130°C

Sorption		Desorption	
time t min.	sorption C_F m.mol./g.	time t min.	sorption C_F m.mol/g.
0	0	0	1.231 (§)
2	0.205	3	1.162
16	0.513	23	1.124
30	0.718	80	1.060
60	0.923	140	1.047
90	1.060	180	0.992
120	1.197		
158	1.368		
180	1.436		
210	1.471		
265	1.573		

(N.B.:- The desorption in this case was arbitrarily started at a value of a sorption of 1.231 m.mol./g. The results however do not at all affect the general line of reasoning adopted in the discussion.)

Table 65.

Sorption rate of aniline vapour on drawn nylon at 70°C

time t min.	spiral length l cm.	extension cm.	sorption C_F m.mol./g
0	8.338	0.0	0.0
2	8.357	0.019	0.081
10	8.367	0.025	0.107
18	8.380	0.042	0.179
33	8.388	0.050	0.213
40	8.393	0.055	0.236
49	8.390	0.052	0.222
75	8.390	0.052	0.222
90	8.390	0.052	0.222
162	8.400	0.062	0.264

Table 66

Sorption rate of stabilised dry acetic acid vapour on wool variously treated: Temp. of sorption=35°; Temp. of liquid=28°C

Sample I (untreated)		Sample II (acid-treated)		Sample III dyed with Solvey blue B.S.	
time t.min	sorption C_F m.mol./g	time t.min	sorption C_F m.mol/g.	time t.min	sorption C_F m.mol./g.
0	0	0	0	0	0
3	0.097	5	0.154	12	0.014
6	0.068	15	0.386	35	0.029
11	0.097	25	0.685	70	0.135
20	0.230	32	0.984	135	0.256
30	0.340	63	2.100	170	0.278
47	0.546	75	2.665		
60	0.704				

Cp.61 p.70

Table 67.

Desorption rates of stabilised dry acetic acid from wool treated variously. Temp. of desorption = 35°C

Sample I (untreated)		Sample II (acid-treated)		Sample III dyed with Solvey blue B.S.	
time t.min.	sorption C_F m.mol/g	time t.min	sorption C_F m.mol/g.	time t.min	sorption C_F m.mol./g
0	0.704	0	2.670	0	0.278
12	0.592	8	1.715	10	0.229
20	0.582	25	1.469	70	0.192
30	0.559	51	1.336	80	0.171
		75	1.303	215	0.085
				240	0.064

Table 69.

Isotherm for water vapour on drawn nylon at 26°C			
Vap.press. p. mm.	Rel.press. p/p_o	% Sorption	Sorption C_F m.mol./g.
0	0	0	0
1.5	0.05	0.637	0.36
3.	0.11	0.956	0.53
8.	0.296	1.732	0.96
10.	0.372	2.256	1.25
12.	0.445	2.557	1.42
15.	0.55	3.138	1.74

Table 70.

Isotherm for methyl alcohol on drawn nylon at 26°C			
Vap.press. p. mm.	Rel.press. p/p_o	% Sorption	Sorption C_F m.mol./g.
0	0	0	0
16.	0.094	1.315	0.41
28.	0.165	2.174	0.68
40.	0.235	2.527	0.79
48.	0.282	3.185	0.99
53.	0.312	3.690	1.15
62.	0.365	3.540	1.11
77.	0.453	4.196	1.31
82.	0.482	4.296	1.34

Table 71.

Isotherm for ethyl alcohol on drawn nylon at 26°C.			
Vap.press. p. mm.	Rel.press. p/p_o	%Sorption	Sorption C_F m.mol./g.
	0.18	0.95	0.21
	0.28	1.32	0.29
	0.45	4.40	0.96
	0.63	6.80	1.48

Table 72.

Isotherms for water vapour on untreated wool.
Temp. of water = 26°C. Temp. of sorption = 34°C
(Sample I)

1st. sorption		2nd. sorption	
Rel.vap.press. p/p_o	Sorption C_F m.mol/g	Rel.vap.press. p/p_o	Sorption C_F m.mol./g.
0.025	0.449	0.05	0.523
0.063	1.140	0.075	1.74
0.088	1.493	0.138	2.86
0.125	1.659	0.200	3.31
0.163	2.004	0.288	4.01
0.213	2.695	0.388	5.23
0.250	2.971	0.475	5.92
0.575	5.803	0.600	6.97

Table 73.

Sorption isotherm for water vapour on acid treated wool. Temp.of water = 26°C. Temp.of sorption = 34°C
(Sample 2)

1st. sorption		2nd. sorption	
Rel.vap.press. p/p_o	Sorption C_F m.mol/g	Rel.vap.press. p/p_o	Sorption C_F m.mol./g.
0.025	0.639	0.063	1.021
0.050	1.410	0.113	2.045
0.150	2.430	0.238	3.245
0.225	2.810	0.400	4.217
0.300	3.960	0.463	4.778
0.425	4.980	0.600	6.576
0.513	5.940	---	---

Table 74.

Sorption isotherms for water vapour on dyed and deaminated wool. Temp. of water = 26°C. Temp. of sorption = 34°C.

Wool dyed with Solvey blue B.S.		Deaminated wool.	
Rel. pressure p/p_o	Sorption C_F m.mol./g.	Rel. pressure p/p_o	Sorption C_F m.mol./g.
0.025	0.515	0.033	0.862
0.063	1.09		
0.125	1.92	0.148	1.96
0.189	2.53	0.189	2.88
0.250	3.18	0.266	3.35
0.313	3.66	0.345	4.05

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